

RUBBER CHEMISTRY AND TECHNOLOGY

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

OUR MOST VERSATILE VEGETABLE PRODUCT. J. R. Hildebrand.

The February 1940 issue of *The National Geographic Magazine* presents as its leading article this interesting 57-page story of the production and uses of rubber. The article and the illustrations, many in color, stress the multitudinous applications of rubber. Writing for the layman, the author explains the properties of rubber, manufacturing processes, and statistics in an easily understood language. [From the *India Rubber World*.]

CRUDE RUBBER. United States Tariff Commission, Washington, D. C. 37 pages.

This report, issued December 11, 1939, describes the present situation respecting crude rubber, with special reference to the effect of the war on United States imports. The report, which points out that crude rubber was the most important single commodity imported into the United States in 1937, covers rubber regulation; statistics on imports, production, consumption, stocks, and prices; transportation and marketing; American-controlled plantations abroad; exchange of rubber for cotton; substitutes for rubber; and conservation of rubber. [From the *India Rubber World*.]

BIBLIOGRAPHY OF RUBBER PATENTS AND LITERATURE—1938. Compiled by J. J. Berliner & Staff, 225 Fifth Ave., New York City. 8½ x 13 in. 43 pp. Mimeographed. \$3.50.

This bibliography is divided into two sections, one containing approximately 400 references to the technical literature on rubber which appeared during 1938 (and the latter part of 1937) and the other listing approximately 600 patents issued in that year in various countries, including the United States, England and France. No abstracts are given, the references to the literature listing the title of the article, the name of the author, and the issue in which it appeared; and those to the patents giving the patent by title first, then patentee, assignee if any,

and the patent number. Journals given in the literature references are abbreviated with full name (but no addresses) at the end of the bibliography.

There are three immediate impressions by glancing through this bibliography: *first*, the number of references to the rubber literature are incomplete, only approximately 400 references being given out of a possible total of 1400; *second*, the references closely resemble (and in many instances are identical with) those in other available sources; *third*, there is neither a subject nor an author index. Careless editing is also apparent, dozens of errors cropping up in spelling, punctuation, and general layout. In full honesty, we cannot recommend the purchase of this bibliography to any member of the rubber industry. [From *The Rubber Age* of New York.]

RUBBER AND RAILWAYS. Second Edition. Colin Macbeth. Issued by the British Rubber Publicity Association, 19 Fenchurch St., London, E. C. 3., England. 1939. Paper, 5½ by 8½ inches, 216 pages. Illustrated. Copies obtainable free of charge.

The first edition of this book, which appeared in 1931, contained only 61 pages. This second edition, extensively revised and amplified, deals with the utilization of rubber by the railways of Great Britain, France and America. Considerable space is devoted to rubber buffing and draw-bar springs, which, according to the author, utilize about one-third of the total amount of rubber used on railways. Other chapters deal with auxiliary bearing springs, bogie bolster mountings, hose and allied parts, and miscellaneous locomotive parts. A section on rubber in coach-work discusses vestibule diaphragms, draught prevention, seat cushioning and mattresses, upholstery fabrics and flooring. The application of pneumatic tires to railway wheels, as exemplified by the Michelin Rail-Car, and the unique utilization of rubber at various important points on the Bugatti High Speed rail vehicles are also treated in detail. Rubber usage is rapidly increasing in this field, and this book, based on authoritative information, should be of interest to all those connected with this work. [From the *India Rubber World*.]

A. S. T. M. STANDARDS ON RUBBER PRODUCTS. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Pa. Paper, 6 by 9 inches, 210 pages. Price \$1.75.

This compilation, issued under the auspices of the American Society for Testing Materials' Committee D-11 on Rubber Products, provides in their latest form 29 widely used specifications and test methods. Fourteen of the standards pertain to general methods: chemical analysis, sample preparation, tension testing, accelerated aging, air pressure heat testing, abrasion resistance, adhesion, flexing, hardness, indentation, resistance to light checking and cracking, and changes in properties of rubber and rubber-like materials in liquids. Rubber hose and belting are covered in three standards; gloves, matting, and tape in four standards. There are five standards relating to various types of insulated wire and cable. Other standards pertain to rubber cements, sponge and hard rubber products.

Of the 29 items, 20 have been issued as tentative and nine have been adopted as standard. Five of the tentative standards were issued in 1939, while three tentative standards were adopted as standard in 1939. Nine standards and tentative standards were revised in 1939. Thus, this book incorporates much new and important material relating to rubber testing. In addition to the above methods and specifications, a proposed draft of specifications for rubber insulating blankets is included. Other features are an eight-page bibliography which provides references to comprehensive sources of information on the properties and testing of rubber products and membership lists of Committee D-11 and its subcommittees. [From the *India Rubber World*.]

A. S. T. M. STANDARDS ON ELECTRICAL INSULATING MATERIALS. American Society for Testing Materials, 260 South Broad St., Philadelphia, Penna. 6 x 9 in. 320 pp. \$2.00.

The latest edition of this compilation, of service to all those concerned with electrical insulation and related materials, includes seven specifications and tests of insulating varnishes, lacquers and similar products. Five standards cover molded materials and five pertain to plates, tubes and rods, including a method for testing phenolic molded laminated products and tests for thickness of solid electrical insulation. Four methods cover various rubber products, including insulating and friction tape, rubber gloves, and matting. [From *The Rubber Age* of New York.]

A. S. T. M. STANDARDS ON TEXTILE MATERIALS. American Society for Testing Materials, 260 S. Broad St., Philadelphia, Penna. 6 x 9 in. 320 pp. \$2.00.

All of the specifications, tolerances, tests and definitions developed by the A. S. T. M. through the work of Committee D-13 on Textile Materials are included in this 1939 textile compilation. In addition to standards covering identification and determination of cotton fibers, general tests on woven fabrics, asbestos roving, yarns and tape, and test methods on cotton, there are specifications and tests covering hose and belt ducks, cotton goods for rubber and pyroxylin coating, tire fabrics, tire cord and Holland cloth. A valuable part of the book is the abstracts of papers presented at meetings of Committee D-13. [From *The Rubber Age* of New York.]

RUBBER GOODS—MANUFACTURERS—UNITED KINGDOM. United States Department of Commerce, Bureau of Foreign and Domestic Commerce, Washington, D. C. Price 10¢. 14 pages.

This trade list, compiled from data submitted by American consular officers abroad, gives the names and addresses of rubber manufacturers in England, Scotland and Wales. The listing is alphabetical and according to location. In some instances the relative size of the firm in its community is indicated. [From *the India Rubber World*.]

DIRECTORY OF MANUFACTURERS IN AKRON. Akron Chamber of Commerce, Akron, Ohio. 8½ x 11 in. 52 pp.

This is the first of what is intended to be an annual or biennial directory of all kinds of manufacturers located in Akron, Barberton, Cuyahoga Falls and their suburbs. Complete names and addresses of the manufacturers are listed, together with names of officers and data on products manufactured. In addition, the directory includes a cross-indexed list of products, including rubber manufactures. Because of the large number of such products, only the more important classifications were used. Copies of the directory are offered without charge to purchasing agents requesting it on business stationery. [From *The Rubber Age* of New York.]

ROYLE STRAINING MACHINES. (Bulletin No. 410). John Royle & Sons, Paterson, N. J. 8½ x 11 in. 8 pp.

The various types of straining machines, built with herringbone gears, by Royle, are illustrated and described in this bulletin. New features in the machines in recent years are stressed. Complete specifications for six different models are given. Brief reference to the company's line of extruding machines is also made. [From *The Rubber Age* of New York.]

A NEW SCIENTIFIC METHOD OF GRADING AND SPECIFYING RUBBER CARBON BLACKS. Godfrey L. Cabot, Inc., Boston, Mass. 24 pages.

The basis of grading rubber carbon blacks presented in this booklet is based on the premise that the fundamental reinforcing properties of different grades of blacks are revealed only after the effects of rate of curing variations have been eliminated. Nine different grades of Cabot blacks are considered. It is shown that the present practical limits of desirable properties are represented in Grades 1 and 9. The maximum or optimum of each of the following characteristics is reached in either of these two grades: tensile strength, elongation, modulus, hardness, resilience, hysteresis loss, heat generation, abrasion resistance, flex-cracking, tear-resistance, plasticity, electrical conductivity, color, diphenylguanidine adsorption, and volatile content. Other grades of black differ in an orderly progression, and the report points out that the exact grade of carbon black may thus be selected for a particular purpose. [From the *India Rubber World*.]

INDEX TO DU PONT RUBBER CHEMICALS LITERATURE. (Report No. 39-8.) Rubber Chemicals Division, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware. 6½ x 9½ in. 20 pp.

As indicated by the title, this is a comprehensive index to all of the literature issued by du Pont on its rubber chemicals to date. In addition, it includes a complete list of technical reports issued by the company since 1937 by title, as well as the reprints of various technical articles which have been made available by the company in recent years. [From *The Rubber Age* of New York.]

CHEMICALS OF COMMERCE. Foster Dee Snell and Cornelia T. Snell. Published by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 1939. Cloth, 5½ by 8½ inches, 542 pages. Indexed. Price \$5.

Prepared to meet a definite need, this reference volume is intended as a source of information on the composition of actual commercial products. It does not cover all chemical compounds, as a chemical dictionary does, but gives more detailed information than such a source on products of definite trade importance. The price-quotation pages of current trade publications have been used as the principal criterion of what is sold in sufficient quantity to recommend inclusion. The subject matter is covered in 37 chapters, and classification is by type of compound so that closely related substances will occur in the same chapter.

Two pages are devoted to a somewhat elementary and brief discussion of natural rubber. Neoprene and Thiokol, termed "rubber replacements" by the authors, are briefly mentioned, as are also Pliofilm, Pliolite, chlorinated rubber, and rubber substitute. Many of the compounding materials used in rubber manufacture are covered, among them: carbon black, China clay, bentonite, sulfur, zinc oxide and rubber solvents. [From the *India Rubber World*.]

CHEMICAL ENGINEERING CATALOG—1939. Reinhold Publishing Corp., 330 West 42nd St., New York City. 8½ x 11 in. 1026 pp.

Like previous editions, this latest issue of the "Standard Reference Catalog of the Process Industries" is divided into five sections: Alphabetical Index, Trade Name Index, Equipment and Supplies, Chemicals and Raw Materials, and a Technical and Scientific Books Section. The inclusion of complete catalogs, an innovation introduced a few years ago, is continued. A new innovation, however, is the publication of several nomographs and charts supplied by various commercial firms and educational and research institutions, including a motor application

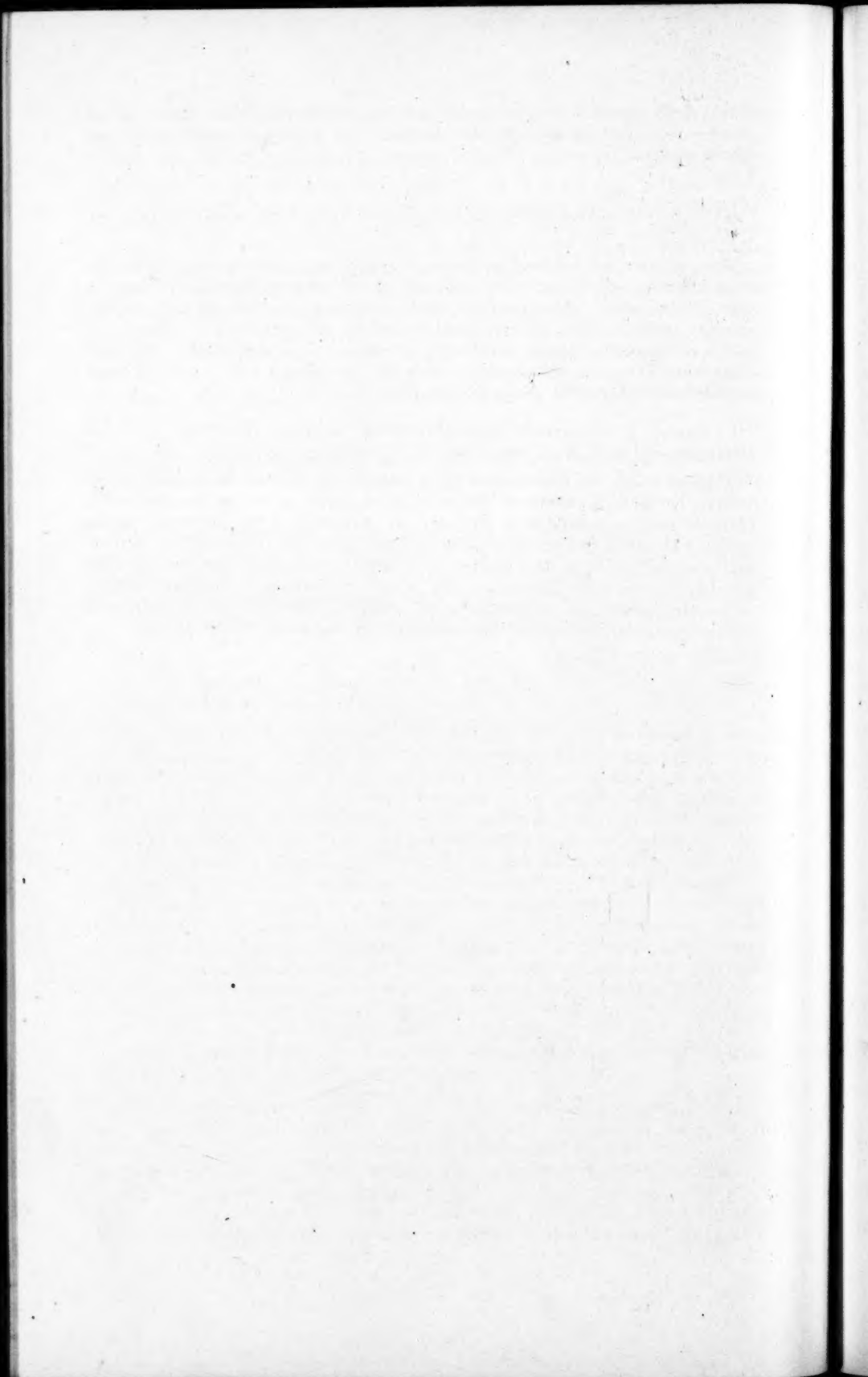
chart for the process industries, tables on belt conveyor design, and charts on fuel losses in coal and oil fired plants. As usual, the catalog is well printed and should continue to serve a valuable purpose. [From *The Rubber Age* of New York.]

RAW MATERIALS BIBLIOGRAPHY. United State Tariff Commission, Washington, D. C. 96 pages.

This bibliography has been prepared in answer to a growing demand for the available literature on raw materials and related subjects, intensified lately by war developments. This literature guide, covering over 200 subjects in this category, contains 728 bibliographical references, all conveniently indexed. Of the 58 references pertaining to rubber, only eight of these deal directly with that commodity. The remainder consider rubber in conjunction with a study of other commodities. [From the *India Rubber World*.]

CHEMICAL INDUSTRIES BUYERS' GUIDEBOOK NUMBER, 1939-1940. *Chemical Industries*, 522 Fifth Ave., New York, N. Y. 660 pages.

This guidebook for the chemical trade includes data on chemical prices, 1934-1938; a list of trade, technical and scientific organizations in all branches of the chemical field; a geographical directory of companies; a raw materials buying guide; a chemical buying guide; chemical specialties for industrial and agricultural uses with a list of their makers; an index of brands and trade names; commercial and scientific synonyms; and a new section on professional services such as consultants, patent attorneys and analysts. The guidebook is distributed with subscription to *Chemical Industries*. [From the *India Rubber World*.]



SOME CAUSES OF VARIATION IN THE QUALITY OF RAW RUBBER AND LATEX *

THE SOL: GEL RATIO IN RELATION TO THE ULTIMATE PHYSICAL PROPERTIES OF RUBBER

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When raw rubber is treated with solvents such as benzene or ether, dissolution is gradual and never complete; a swollen residue remains which disperses extremely slowly, if at all. The soluble portion is generally called the "sol", and the insoluble the "gel", and although these need not be considered as two distinct components, it is convenient, in view of the existing state of our knowledge regarding them, to continue to use this terminology.

The nature of the gel fraction of raw rubber has long been under discussion. Gladstone and Hibbert¹ were inclined to regard the less soluble modification as a product produced by heat during the drying of the latex and rubber, whereas Fessenden² and Seeligman³ came to the conclusion that the two components were isomerides, a view which has long persisted. Weber⁴, as the result of studies of the gel fraction of Para rubber, contended that the soluble and insoluble fractions were not identical in composition. Later it was shown by one of us⁵ that the gel fraction contained proteins which could be removed only by suitable treatment of the latex before coagulation or by digestion of the rubber in presence of acids or alkali⁶. These early observations and records are of more than historical interest, as they foreshadow in large measure almost all that has been made known regarding the origin and nature of the gel fraction in raw rubber. The vast array of recent literature on this subject is admirably reviewed in the English edition of Memmler's "Handbuch der Kautschukwissenschaft"⁷.

Although the true nature and practical importance of the insoluble (gel) fraction of raw rubber are matters on which a great deal of work still remains to be done, it has become evident that the sol and gel fractions can hardly be regarded as fixed and definite components of identical composition, and that their presence together in raw rubber may be fortuitous, for it has been shown that the sol fraction of raw rubber is readily converted under suitable conditions into a product which, if not identical with the gel, has nevertheless all its known properties. Thus in the more or less complete absence of oxygen or in light, the sol fraction is rendered insoluble and more tough and less extensible than the parent material. Staudinger in a recent communication⁸ has again attempted to give expression to the change taking place in this transformation, which is not, after all, an isolated phenomenon⁹, by suggesting that the sensitive thread-like molecules of the original rubber hydrocarbon are converted into three-dimensional macromolecules. A similar explanation was offered by us^{10, 12} as the result of our studies of neutral latex exposed to sunlight in the presence of traces of quinones and a variety of other reagents. Here we showed that the sol:gel ratio in latex

* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 58, No. 12, pages 345-351, December 1939.

or rubber may be altered so that almost the whole of the rubber is rendered insoluble. This conversion of sol into gel, however, is measurably reduced by the presence of molecular oxygen and, in the case of certain of the reagents employed, an actual depolymerization takes place if oxygen is not excluded. In the present communication evidence is presented to show that transformations from sol to gel (enhanced polymerization) or, alternatively, from gel to sol (depolymerization) actually take place in the preparation of raw rubber as a practical matter¹¹.

That the soluble and insoluble portions of raw rubber possess different physical qualities was demonstrated by work at the U. S. Bureau of Standards, where purified rubber was fractionated with ether with great care and elegance. The gel fraction was found to be tougher and more difficult to break down on the mill (plasticize) and the rubber presented a gristle-like appearance after compounding. The stress-strain curves of vulcanizates prepared in the customary way from the sol fraction were different from those of the gel, which apparently cured more rapidly and was stiffer throughout. Vulcanizates of the unfractionated material were intermediate between the two¹³.

The present paper contains the results of a study of the mechanical properties of rubber of varying gel content formed by the action of sunlight on latex containing a small quantity of 1,4-naphthoquinone or of benzaldehyde. It is clear that the changes in solubility gradually brought about by the continued action of sunlight on latex containing such reagents are accompanied by marked alterations in mechanical properties, decreased solubility and swelling running parallel with increased breaking strength. The fact that these differences are not apparent to the same extent in samples subsequently vulcanized in the ordinary way is not surprising. Profound changes in the complex structure of rubber, as the result of milling, undoubtedly occur to an extent which cannot possibly be accurately controlled or measured. In the preparation of rubber for vulcanization, as at present carried out, variations in original quality may be completely obscured, more particularly if the samples are broken down to the same degree of plasticity, as is customary for milling purposes. That differences in structure and in physical behavior still obtain after vulcanization is evidenced by results here recorded on the swelling properties of vulcanizates prepared directly from latex previously subjected to the action of benzaldehyde in sunlight. By employing this reagent as a "bridge-builder" for enhanced polymerization in the absence of air on the one hand and as a "chain-breaker" for depolymerization in the presence of air on the other, products with varying solubility and swelling properties have been obtained. When these transformations are brought about in one and the same sample, vulcanizates prepared directly from the same have much less tendency to swell, imbibing Diesel oil, for example, to only a limited degree compared with vulcanizates prepared from the original, untreated latex rubber. A way would now seem to be opened up for the preparation of modified rubbers, as depicted by Rideal¹⁴, whereby the physical structure of natural rubber may be so modified that vulcanizates can be produced having less of the swelling properties of vulcanized, natural rubber and more of the structure and physical character of synthetic rubbers, the swelling and other physical characteristics of which are well known.

EXPERIMENTAL

Material.—The material used in all these experiments was *Hevea* latex buffered at pH 6.8-7.1 with phosphate buffer and sterilized immediately after collection in the Far East (E), and commercial latex from which the ammonia and other

diffusible substances were removed by dialysis against 0.05M neutral phosphate buffer on arrival in the United States (*G*). Both materials were sterilized in sealed containers practically filled to capacity¹⁵. Samples were coagulated by adjusting the pH to 4.8 with 10% acetic acid, unless otherwise indicated. The rubber in every case was extracted by repeated treatment with fresh acetone in the cold and dried *in vacuo*, all operations being conducted in the dark room. Solubility and swelling tests were carried out by the procedure previously described^{10, 12}.

CHANGES IN THE SOL: GEL RATIO OF LATEX IN STORAGE AND TREATMENT

Transformations in storage.—Samples of latex *E*, sterilized in sealed containers immediately after collection in the Far East, have been examined and found to contain less than 20 per cent of gel. Various samples of commercial 40 per cent latex and 60 per cent concentrate, containing ammonia, examined immediately on arrival here, have been found to contain nearly twice this amount, or on the average 40 per cent of gel substance. Furthermore, the sol:gel ratio of the sterile latex *E* has remained constant, some of the sample cans being now over three years old. In the case of commercial latex, not only does the gel content vary greatly with the source¹⁶, but there seems to be a progressive increase with time. That the comparatively low gel content of the neutral, sterile latex prepared at the source is not the result of sterilization is clearly demonstrated by the fact that repeated sterilization makes no measurable change in the sol:gel ratio if it is carried out as has been indicated. As it is already well known that the mechanical properties of rubber from ammonia-preserved latex vary with the age of the latter, it is significant, to say the least, that we should now find wide variations in sol:gel ratio and a gradually increasing proportion of gel in these commercial products. In the absence of authentic records of origin and treatment of our various commercial samples, we have not seen fit to investigate this matter further¹⁷. This work can better be undertaken at the source, where, with fresh latex to start with, solubility data of great significance may be obtained, particularly if at the same time physical measurements are made on test slabs prepared directly from the latex samples on porous tiles.

TRANSFORMATIONS IN COAGULATION BY ACID

Samples of latex *G* and of commercial latex concentrate were coagulated by adding just enough acetic or sulfuric acid to bring the pH from 6.8 to 4.8 or by

TABLE I

Series	Latex coagulated in various ways Proportions soluble in benzene in 14 days			
	Samples			
	1	2	3	4
Tile coagulation	0.37	0.47	0.42	0.45
Acetic acid coagulation.....	0.64	0.53	—	0.50
Sulfuric acid coagulation.....	—	0.68	0.64	—
Sulfuric acid coagulation (two-fold excess).....	—	—	0.83	—

pouring on tiles of unglazed porcelain. The coagula were extracted with acetone for solubility measurements made as previously described.

The results, given in Table I, are in line with the effect of acids in general on rubber⁶. Former conclusions that minimal quantities of sulfuric acid or acetic

acid in moderate excess do not affect the rubber have been based on comparisons of samples broken down on the mill for vulcanization test purposes¹⁸, a much less sensitive criterion, as already pointed out.

TRANSFORMATIONS BROUGHT ABOUT BY BACTERIA

In a previous publication¹⁹ it has been shown that the rubber hydrocarbon in latex is readily attacked by common aerobic bacteria isolated from garden soil. The consumption of a portion of the rubber, which is converted (*inter alia*) into water-soluble products, is accompanied by marked changes in the solubility of the remainder of the rubber, as illustrated by the following experiment taken from a comprehensive study of the process of bacterial decomposition of rubber to be published elsewhere.

Eighteen Erlenmeyer flasks each with 190 cc. of tap-water containing 0.01M-Sørensen neutral phosphate buffer mixture, 0.1 per cent of potassium nitrate and 0.01 per cent of magnesium sulfate, were sterilized. To each flask 7 cc. of a neutral, sterile latex of approximately 30 per cent dry rubber content were then added with aseptic precautions. Nine of the flasks were inoculated with 3 cc. of a suspension of a pure culture of *Actinomyces*. The methods for preparation of the neutral sterile latex and for the isolation of strains of *Actinomyces* in pure culture from garden soil have already been described¹⁹. All of the flasks, with the exception of two retained for immediate analysis, were incubated at 30°. At various intervals of time, up to 54 days, flasks were removed for analysis and solubility measurements. The various samples were coagulated completely by the addition of the necessary few drops of dilute acid to bring the pH to 4.8. Each coagulum was filtered from the watery serum, extracted with 95 per cent alcohol repeatedly in the cold, and dried *in vacuo* in the dark over calcium chloride.

To determine the extent of bacterial growth in the inoculated latex and for solubility test purposes, 0.5 gram of each coagulum was first dissolved in 25 cc. of benzene containing 1 per cent of trichloroacetic acid. After 48 hours in sunlight the rubber was completely broken down in this way so that the benzene solution could be readily filtered through a sintered glass crucible and the bacteria and (or) protein washed with benzene, dried and weighed. Solubility measurements were carried out in pure benzene by the method previously described, due allowance being made for the bacteria and protein present in each sample.

The results, given in Table II, show not only a marked change in solubility brought about by very short periods of incubation (3 days), but also the gradual conversion of the residual rubber into a product swelling but no longer dissolving in benzene. In the sterile controls, on the other hand, the reverse result is to be seen in a slight but consistent increase in solubility due, no doubt, to depolymerization of the rubber by protracted exposure to air. Data in relation to the rate of growth of this particular organism, including the rubber consumed, are also given as of vital interest, but a discussion of their significance is reserved until a full account of the metabolic activity of this organism and of the water-soluble products of the decomposition of rubber hydrocarbon can be undertaken. It should be pointed out here that the products resulting from the coagulation of the sterile latex samples became more plastic than the original rubber as incubation proceeded. The inoculated latex, on the other hand, produced coagula which became progressively harder and darker in color on drying. After 24 days the coagulation of the inoculated latex resulted in a product which, although still somewhat elastic, was hard and tough at room temperature, and resembled balata far more than rubber.

TABLE II
CHANGES IN SOLUBILITY OF RUBBER BROUGHT ABOUT BY BACTERIA IN LATEX

Period of incubation at 30° in days	Sample	Latex coagulum wt. in g. (alcohol-extd.)	Bacteria and (or) protein wt. in g. (benzene-extd. and dry)	Loss of rubber g. 2.074 Ave. of original R	Proportion of residual rubber soluble in benzene in 14 days
0	Controls	2.1030	0.0336	0	0.84
		2.1137	0.0338	—	0.83
3	Sterile	2.1089	—	0.0459	0.77
	Inoculated	2.1102	0.0814	0.1767	0.63
6	Inoculated	2.0321	0.1341	—	—
10	Sterile	2.1085	—	0.2604	0.59
	Inoculated	1.9433	0.1380	—	—
13	Sterile	2.1113	—	0.0317	0.53
	Inoculated	1.8779	0.1472	—	0.54
17	Inoculated	1.8580	0.1624	0.3791	—
24	Sterile	2.0880	—	—	0.48
	Inoculated	1.7640	0.0330	0.0197	0.90
38	Sterile	2.1106	—	0.4853	0.88
	Inoculated	1.5952	0.0363	—	—
45	Sterile	2.0902	0.1085	0.6480	0.46
	Inoculated	1.6056	0.0359	—	—
54	Sterile	2.1018	0.1465	0.6156	0.47
	Inoculated	1.4970	0.0353	0.7263	0.45
			0.1486	—	—

TRANSFORMATIONS BY SMOKING: EFFECT OF LIGHT AND HEAT

The marked conversion of sol into gel, accompanied by improvements in mechanical properties, produced by light in the presence of traces of quinones, aldehydes and ketones¹⁰ suggested that the action of light may play a part in the coagulation of latex by the still unexcelled and now classic method for the preparation of Para rubber, in which wood smoke, well known to contain compounds of this type, is employed.

Latex G, of 38 per cent rubber content, was coagulated by smoke from a smouldering fire composed of partly dried oak chips, fern leaves and pine cones. A glass rod was first dipped in the latex and then slowly rotated in the smoke; this procedure was repeated through a period of 80 minutes or until a thick film had been formed on the glass rod. The operation was conducted in sunlight in the first instance, and repeated with a fresh sample of the same latex in the dark the evening of the same day. The coagula were dried in the dark room and solubility measurements made in the usual way (Table III).

TABLE III

Treatment	Proportion soluble in 14 days	Swelling index
Smoked in darkness.....	0.61	108
Smoked in light.....	0.38	55

The significance of these results as a practical matter in the treatment of latex by smoking is apparent.

In an experiment to demonstrate the possible effect of such substances on rubber itself, thin sheets of fresh latex crepe were exposed in the laboratory to the vapor of benzoquinone (a) in sunlight, and (b) in darkness. The sheets were placed with a few crystals of benzoquinone in two large covered Petri dishes, the rubber resting on a clock glass, benzoquinone in the Petri dish itself. One Petri dish was completely blackened on the outside. After 48 hours under these conditions the rubber samples were removed. One-half of each sample, now a rich, reddish brown, resembling ribbed-smoked sheet, was finally heated for 3 hours at 105° in a sealed glass tube, first filled with nitrogen and evacuated. Solubility measurements were made on the four samples, after acetone extraction and vacuum drying. The proportion soluble in 14 days in benzene was as follows: exposed to benzoquinone vapor in sunlight, 0.39; exposed to benzoquinone vapor in dark, 0.74; exposed to benzoquinone vapor in sunlight and then heated in absence of air, 0.40; exposed to benzoquinone vapor in dark and then heated in absence of air, 0.61. These results show a marked change in the sol:gel ratio in sheet rubber exposed to the action of light in presence of the vapor of benzoquinone or, after absorption of benzoquinone, heated in absence of air.

In a subsequent experiment to test the effect of sunlight on rubber previously exposed to the vapor, samples of unsmoked sheet (2 mm. thick) and of thin, pale crepe (1 mm. thick) were exposed overnight to the vapor of benzoquinone in a large desiccator and then to the action of sunlight for 3 hours. Solubility measurements were made in this case on the unextracted samples. The results are given in Table IV.

The gel in the light-exposed samples was sharply defined and the rubbers were firmer and much more difficult to break down on the mill than the untreated controls.

These various experiments serve to show additional sources of possible variation in the solubility and mechanical qualities of raw rubber as a practical matter.

TABLE IV

Material	Treatment	Proportion soluble in 14 days	Swelling index
Unsmoked sheet	Control untreated	0.81	85
Unsmoked sheet	Exposed to benzoquinone vapor, then to sunlight	0.61	56
Pale crepe	Control untreated	0.46	55
Pale crepe	Exposed to benzoquinone vapor, then to sunlight (3 hrs.)	0.31	33

EFFECT OF ALKALI ON ENHANCED POLYMERIZATION

In these, as in all preceding studies, only neutral latex has been employed. Investigations over the past three years have shown that the enhanced polymerization brought about by the action of those reagents to which we have referred in detail elsewhere^{10, 12} is adversely affected not only by substances present in the serum of natural latex but also by others, such as peroxides, and more particularly by alkali, which is added to all commercial latex for its preservation. This effect of alkali is clearly illustrated by the following examples. Whether the

TABLE V

Material	Proportion of rubber soluble in 14 days	Swelling index
Original latex, containing ammonia	0.15	25
Latex, ammonia-free	0.05	10
Latex containing NaOH (pH 10)	0.44	100

TABLE VI

Material	Proportion of rubber soluble in 14 days	Swelling index
Latex pH 7.2	0.06	11
(1) Latex pH 10 (by ammonia)	0.11	18
(2) Latex pH 10 (by caustic soda)	0.37	63

polymerization is carried out by light or by heat, there is a lowering of the overall enhancement when alkali is present. If access to air is also permitted, the net result may be an accelerated depolymerization of the rubber.

A 60 per cent latex concentrate was completely freed from ammonia by repeated dialysis against 0.05*M* neutral phosphate buffer. Dilute caustic soda solution was then added to part of this purified latex until a pH of 10 was attained. All samples were diluted to 15 per cent rubber content and exposed to sunlight for four hours with 0.06 per cent of 1,4-naphthoquinone in closed glass tubes. The latex, after exposure, was coagulated on porous tiles in the dark room. The solubility and swelling data are given in Table V.

Freshly dialyzed commercial latex (pH 7.2), diluted to 15 per cent rubber content, was brought to pH 10 by addition of (1) ammonia or (2) caustic soda. All samples were exposed to sunlight for 4 hours in presence of 0.06 per cent of 1,4-naphthoquinone, in closed glass tubes on a rocking machine. The latex was coagulated on porous tiles and solubility measurements were made in the usual way (Table VI).

To samples of sterile latex *E*, diluted to 20 per cent rubber content, sufficient ammonia or caustic soda was added to bring the pH to 9.0 and 12.0 respectively. After addition of 0.2 per cent of benzoquinone to each sample, they were exposed to sunlight for 3 hours, in closed tubes. The solubility and swelling data are given in Table VII.

It is seen that the enhanced polymerization brought about by benzoquinone in neutral latex is almost completely lost in presence of alkali.

TABLE VII

Treatment	Proportion of rubber soluble in 14 days	Swelling index
Latex untreated, pH 7.2.....	0.82	111
Sun-exposed with benzoquinone		
pH 7.2	0.38	38
pH 9 with ammonia.....	0.83	93
pH 12 with ammonia.....	0.84	94
pH 9 with caustic soda.....	0.83	103
pH 12 with caustic soda.....	0.86	105

PARALLEL SOLUBILITY AND TENSILE-ELONGATION MEASUREMENTS

To 350 cc. of neutral latex *G* of 34.5 per cent rubber content, 1.2 gram of 1,4-naphthoquinone was added. The naphthoquinone was dissolved in 25 cc. of warm alcohol into which 75 cc. of water were poured just before adding to the latex. After thorough stirring, this latex was divided into seven equal parts, all operations being conducted in the dark room. The samples, placed in individual glass tubes filled almost to capacity and well closed, were exposed to sunlight on the table of a rocking machine on the roof of the laboratory. At various intervals of time, up to 10 hours, a sample tube was withdrawn and returned to the dark room, where it was allowed to remain for several hours to permit gas bubbles to escape before opening and pouring the contents of the tube on a porous tile. An extra sample of this same latex, but containing no naphthoquinone, was poured directly on a tile in the dark room.

The individual sheets of rubber were dried at room temperature in the dark room, a small sample of each being extracted with acetone in the cold for solubility and swelling tests. Tensile-elongation measurements were made in duplicate on strips punched from the original sheets and tested in the usual way. The proportion soluble in 14 days, the swelling index and the tensile strength are plotted in Figure 1. The elongation at break showed no trend and was sensibly constant, varying only from 1075 to 1015 per cent among the samples.

It is clear that the changes in solubility brought about by the action of sunlight in presence of naphthoquinone are accompanied by important alterations in physical properties, decreased solubility and swelling running parallel to increased breaking strength. The five-fold increase in tensile strength, after ten hours' exposure, accompanied by no appreciable reduction in elongation, marks the transition of raw rubber of poor quality into a product having the tensile-elongation properties of the best, air-dried fine Para rubber.

To discover to what extent such alterations in the quality of raw rubbers are reflected in their vulcanizates after milling and compounding, 1160 cc. of latex *E* were exposed for 5 hours to the action of sunlight in large glass tubes on the shaking machine, 1 per cent of 1,4-naphthoquinone (on the weight of rubber) having been previously added as before. After treatment in this way, the latex was poured on large porous tiles and the rubber coagulum finally dried at room temperature, all in the dark room. 775 cc. of the same latex, untreated, were poured on separate tiles, the rubber therefrom serving as a control. Solubility measurements in benzene were made on small acetone-extracted samples. The dry rubbers were finally broken down on the mill and compounded in the usual way and on the following test recipe: rubber 100, zinc oxide 133.5, sulfur 4, litharge 12.5. Slab cures for various periods were made in the press at 290° F. Solubility figures and stress-strain data are summarized in Table VIII.

The differences in mechanical properties of the two samples are of the same general order as those observed by Smith and Holt¹³, of the Bureau of Standards,

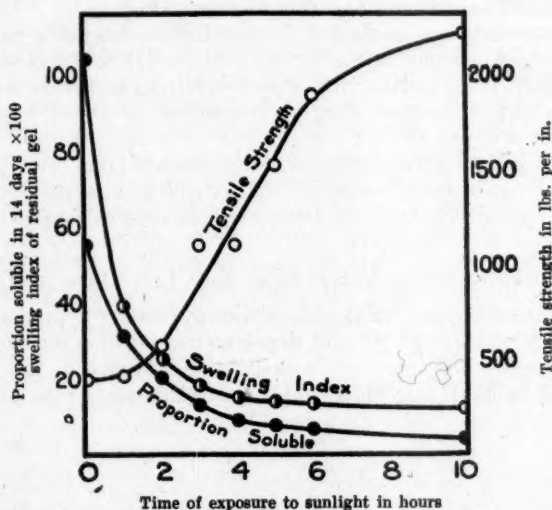


FIG. 1.—Latex treated with naphthaquinone in sunlight.

TABLE VIII

Treatment of latex	Proportion of rubber soluble in 14 days	Swelling index	Mechanical properties			
			Press cures at 290° F. (minutes)	Stress at 800%	Elongation at break (%)	Tensile strength (lb. per sq. in.)
Latex untreated (control).....	0.84	101	9	283	610	1400
			20	468	700	2323
			30	605	620	2437
			45	622	600	2319
Latex, with naphthaquinone, exposed for 5 hours to sunlight	0.28	56	9	409	680	2030
			20	605	660	2487
			30	682	620	2388
			45	698	600	2127

TABLE IX

Material	Time of cure at 290° F. (minutes)	Percentage increase in weight in Diesel oil at 40° C.				
		24 hrs.	2 days	3 days	6 days	9 days
Untreated rubber	20	94	132	143	162	174
Modified rubber	—	81	107	113	122	128
Untreated rubber	30	79	109	118	129	134
Modified rubber	—	60	84	91	96	100
Untreated rubber	45	73	97	105	115	120
Modified rubber	—	58	79	85	90	93

for vulcanizates of the sol and gel fractions of raw rubber, the rubber from the treated latex showing increased rigidity throughout and reaching its optimum cure more rapidly than the untreated control. The behaviors of the two materials on the mill were very different; the treated rubber was far tougher and took

approximately twice as long to reduce to the same plasticity as the control. Undoubtedly this prolonged milling of the treated sample, with consequently more complete breakdown of the structure, reduced the differences in their ultimate quality, determined by tensile-elongation measurements.

On general considerations it seemed worth while to determine whether differences in the swelling behavior of the two materials could be detected after milling and vulcanization. Discs of the vulcanizates were punched from slabs and were weighed before and after immersion, by suspension, in Diesel oil at 46°. The results are given in Table IX.

These differences in swelling behavior, although not large, are consistent and significant. They have been confirmed and extended in studies of simple vulcanizates prepared directly from the latex itself, as described below.

SWELLING PROPERTIES OF VULCANIZATES FROM LATEX-TREATED RUBBER

Employing benzaldehyde, which, as previously shown¹⁰, produces enhanced polymerization in absence of air and depolymerization in presence of air, two quantities of latex *E* were exposed to sunlight in presence of this reagent (2.5 per cent on the rubber) for 5 hours (1) in a sealed glass tube evacuated and

TABLE X

Treatment Neutral latex with benzaldehyde exposed to	Before vulcanization with sulfur		After vulcanization with sulfur (45 min. at 98°)	
	Proportion soluble in 14 days	Swelling index	Proportion soluble in benzene in 14 days	Swelling index
(a) Sunlight in nitrogen.....	0.15	16	0.016	11
(b) Sunlight in air.....	Completely dissolved after 3 days	—	0.38	37
(c) Sunlight in nitrogen, then in air. 0.41		40	0.021	11

filled with nitrogen and (2) in a large flat dish with cover open to the air; one-half of the sample (1) was then exposed again for an additional five hours in presence of air (sample 3). To each of these samples, sulfur and zinc butylxanthate were added in the form of aqueous dispersions in amounts equivalent to 1 per cent of the rubber in latex. The samples were coagulated as thin films on large porous tiles. Solubility and swelling measurements were made on acetone-extracted samples before and after vulcanization under water at 98° for 45 minutes. The results are given in Table X.

The appearance of the rubbers was as follows: (1) a very tough, snappy elastic sheet both before and after vulcanization; (2) plastic and soft before vulcanization, short and lacking strength thereafter; (3) much less plastic than (2) before vulcanization, short but tough elastic sheet thereafter. It is important to note that the swelling properties of the modified rubbers are carried over into their sulfur vulcanizates.

This test was repeated on a larger scale for the purpose of swelling measurements in Diesel oil made on vulcanizates prepared from treated latices. Benzaldehyde was again employed (2.5 per cent on the rubber) for both enhanced polymerization and depolymerization. The vulcanizates were prepared in this series by mixing with the latex, after treatment, a fresh dispersion of compounding materials in the following proportions per 100 parts of rubber: P-33 black 20,

zinc oxide 3, zinc butylxanthate 1, sulfur 1. Discs 0.0625 inch thick were vulcanized in a monel-metal mould at 105° C. for 20, 40 and 60 minutes. Swelling measurements were made by suspension of the vulcanized discs in Diesel oil at 46° for various periods of time up to 16 days. The results are expressed in terms of the original weight of the discs, in Table XI.

Those rubbers previously treated with benzaldehyde show much less swelling than the controls, especially the samples which had been subjected to both enhanced polymerization and breakdown.

It will be obvious from our previous publication¹⁰ that in many cases heat may be advantageously employed to bring about similar transformations. Thus rubber when heated with benzoquinone or with benzoyl peroxide in the absence of air undergoes enhanced polymerization, whereas, in presence of air, breakdown of the molecule takes place. Similarly, one reagent may be employed to bring about polymerization, whereas other means may be more useful in effecting depolymerization²⁰. The best conditions of treatment and for achieving minimum

TABLE XI

Treatment	Percentage increase in weight in Diesel oil at 46°			
	2 days	4 days	8 days	16 days
Vulcanization 20 min. at 105°	2 days	4 days	8 days	16 days
Untreated control	236	247	257	—
Polymerization	210	220	227	—
Depolymerization	212	220	226	—
Polymerization, then depolymerization..	169	175	179	—
Vulcanization 40 min. at 105°	2 days	4 days	8 days	16 days
Untreated control	226	239	249	—
Polymerization	200	215	222	—
Depolymerization	201	216	224	—
Polymerization, then depolymerization..	153	165	171	—
Vulcanization 60 min. at 105°	2 days	4 days	8 days	16 days
Untreated control	224	244	255	277
Polymerization	196	211	219	233
Depolymerization	197	222	232	245
Polymerization, then depolymerization..	159	169	173	181

swelling have still to be developed, but these results broadly illustrate means by which the production of vulcanized rubber having the swelling and other physical characteristics of the best synthetic rubbers may yet be attained.

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EFFECT OF VULCANIZATION ON RUBBER STRUCTURE

A PROBLEM IN PROBABILITIES *

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In Goodyear's day, the problem of understanding the process of vulcanization could be expressed by the question: "Why does heating rubber with sulfur keep it from getting soft and tacky on a hot summer day, and hard and boardy in cold winter weather?"

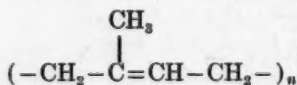
The deceptive simplicity of this question probably inspired the hope, which has come down almost to the present day, that the secrets of vulcanization and even of the elasticity of rubber could be explained in terms of the properties and reactions of simple organic molecules, such as the reactions of sulfur with simple olefins. The vast increase in the knowledge of giant molecules during the past decade has shattered any basis there may have been for such a hope, but occasional articles show that this desire for simplicity continues to live and to color our thinking on this problem.

This paper discusses some of the inherent limitations of the old, simpler pictures of vulcanization and the structure of rubber, and some of the implications of the present view that crude rubber is built up of giant molecules. Probably there are not merely one or two or half a dozen reactions, but rather there are literally millions of possible vulcanization reactions, each of which may influence the physical properties of the rubber. The study of these reactions will require new and far more sensitive methods of physical and chemical analysis than have been available heretofore, as well as new points of view in interpreting the data.

STRUCTURE OF CRUDE RUBBER

The problem of finding what changes occur in the structure of rubber during vulcanization requires first some knowledge of the structure of crude, unvulcanized rubber.

From the standpoint of classical organic chemistry, the formula for polyisoprene:



adequately expresses the structure (or chemical properties) of highly purified rubber¹². It predicts carbon-hydrogen ratios that are checked by experiment within a few tenths of a per cent¹³ and unsaturation values that are verified within about one-half per cent, as well as the approximate composition of reaction products with ozone, sulfur, chlorine, etc. It has been assumed¹³ that if n is large, as osmotic pressure, viscosity¹⁴, and ultracentrifuge¹⁵ tests show it to be, then the question of whether the chains form closed rings or are open at the ends is not of great significance.

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This formula does not explain a number of different properties of crude rubber which are of interest and importance to rubber technologists, such as the observed dipole moments of rubber in solutions³⁰, the effect of the drying of rubber on the viscosity of its solutions³¹, or the effect of traces of piperidine on the viscosity. Nor does it explain why purified crude rubber can be separated by diffusion processes into two more or less definite fractions—sol and gel rubbers—which have about the same ultimate chemical analysis³²; nor why gel rubber eventually goes into solution if given enough time in contact with air; nor why, when solutions of gel rubber are cooled, the crystals formed have different melting points (-1.5° to $+10^{\circ}$ C. or $+29.3^{\circ}$ to $+50^{\circ}$ F.) from those obtained from solutions of sol rubber ($10 \pm 1^{\circ}$ C.). Fractional precipitation tests³³ show that purified sol rubber is composed largely of a single component, but milled or degraded rubbers can be separated into a great many different fractions. At one time³ it was assumed, on the basis of the above formula, that the degree of polymerization could be lowered by milling or "degrading" the rubber or even by raising its temperature, and that the reverse process occurred on standing or cooling. It is known now that the different types of breakdown during mastication involve oxidation of the rubber⁸.

When it was found that the size of the rubber molecule in solution was very large, not only did the problem of determining its structure become much more complicated, but new factors entered which made it almost a different kind of problem.

In the first place, the accuracy of the chemical analysis required to establish the essential chemical structure was increased enormously. To detect the hydrogenation of one double bond in a polyisoprene chain of 10,000 or more carbon atoms by analysis of the carbon-hydrogen ratio would require an accuracy better than that obtained in atomic weight work. Actually, the best determinations of carbon-hydrogen ratios of purified crude rubber, made at the National Bureau of Standards, usually totaled about 0.2 per cent less than 100 per cent (probably due to combined oxygen in the rubber). Even when this discrepancy is ignored, it is stated³⁴ that the results make possible "identifying the rubber hydrocarbon as a polymer of C_5H_8 , only provided it has less than 100 carbon atoms". By means of similar tests Midgley and co-workers³⁵ also found oxygen in rubber and concluded that it might be a homolog of geraniol. Identifying the enormous number of possible isomers that might be formed is far beyond the range of any available tests.

It may be concluded on the basis of these chemical tests that the rubber which enters the vulcanization reactions is not polyisoprene. Instead, it is probably made up of a number of substituted or modified isoprenes, perhaps having some branched chains and some cyclization. Because of the uncertainty about the structure of crude rubber and the tremendously large number of isomers that may be formed, it is necessary to consider the study of vulcanization reactions as a problem in probabilities.

Another result of a large increase in the molecular weight is to reduce the chemical effects obtained from substituting one group per molecule; *e. g.*, the acidity of the compounds $CH_3(CH_2)_nCOOH$ decreases as n increases. However, if the molecular weight is high, substitution of one group in a molecule may have very great effects on certain physical properties such as viscosity, plasticity and tensile strength. The association or reaction of the carboxyl groups of different molecules, in acetic or benzoic acid for example, has comparatively little effect on the viscosity of their solutions, even though it may effectively double the mole-

cular weight. However, if this type of reaction occurred with a material whose molecular weight was initially 100,000 or 1,000,000, the physical effects of doubling the molecular weight might be enormous. Here, as in some of the vulcanization reactions, physical tests may be much more sensitive (and useful) than chemical tests in studying changes of structure.

Another property, high elasticity (or extensibility), is made possible by a high molecular weight; and the study of the elastic behavior, in turn, enables us by geometric and thermodynamic reasoning to make a number of inferences about the size and shape of the molecules of crude and vulcanized rubber. This type of attack on the problem will undoubtedly become more important in the near future.

The fact that rubber can be stretched almost reversibly up to, say, 900 per cent with very little change in density shows⁷:

1. The rubber must contain strong filaments which are normally crumpled or twisted to less than one-tenth their extended length.

2. These filaments can slide past one another with very little friction over most of their length, *i. e.*, they have weak or uniform secondary valence forces.

3. At a few points they are interlocked or held together in a two- or three-dimensional network, to limit the degree of deformation or flow. This may be by primary valence bonds, as at sulfur bridges in cured rubber, by secondary valence forces at polar groups, or perhaps even by secondary valence bonds along the normal chain, as in rubber crystals.

4. There is some mechanism that tends to make the filaments and network return substantially to their original crumpled state after the external stress is removed. A number of energy factors may contribute to this process, *e. g.*, attraction of hydrogen atoms (Mack), attraction of double-bonded carbon atoms (Fickentscher and Mark), and relief of the slight distortion produced in valence angles by stretching. Recently it has been recognized^{7, 11, 20, 21, 22, 26} that a more important factor causing retraction is the tendency of the chains to assume positions of maximum randomness, or maximum entropy.

This effect can be visualized by considering a long thread suspended from the ceiling with a small weight at the lower end. If the thread is coated with Tangle-foot adhesive and a swarm of flies alights on the thread, then the efforts of the flies to escape in all directions will make the thread assume irregular zigzag shapes. These irregular shapes will require shorter distances between the ends of the string and thus raise the weight. Brownian motion of the atoms in the rubber filaments, causing rotation around single valence chains, produces the random distribution and increase in entropy that makes the rubber samples retract.

It follows from this simple picture that, when rubber is stretched to a given elongation, the tension should vary directly with the absolute temperature. This was confirmed by Meyer²⁶ for a high-sulfur compound, but usually other factors such as flow, hysteresis, crystallization, etc., complicate the process. It would seem that a study of the deviations of the stress from the predicted relations would offer a new and fruitful method of studying the structure of crude and vulcanized rubber.

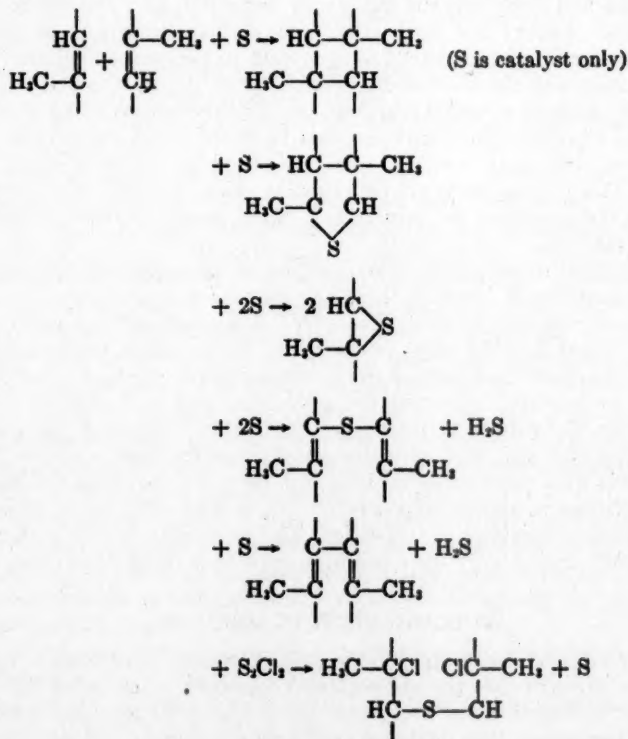
Since physical tests show that the crude rubber molecule is not only very large but also elastic, the problem of vulcanization becomes even more complicated, for it is necessary to consider the possibility of intra- as well as intermolecular reactions.

The following sections of this paper will discuss the changes in structure produced by vulcanization.

LIMITATIONS OF CLASSICAL THEORY OF VULCANIZATION

The change of rubber during vulcanization from a soft plastic material to a highly elastic solid, or from a solution to a gel, presumably requires the development of cross bonds between the rubber molecules to form some kind of a three-dimensional network structure^{25, 31, 33, 38, 39, 40}. Qualitatively, almost any kind of cross bonds would be satisfactory to form the networks, either direct C—C bonds, C—S—C or C—O—C bridges, the secondary valence forces around groups such as C=S, C=O, etc., or even the mechanical interlocking or association of the hydrocarbon groups. However, no explanation has been given which even qualitatively accounts for the progressive physical changes through the course of the vulcanization processes, including the overcures. With the new methods and viewpoints developed in recent years, a concerted attack on this problem by the whole rubber industry might show considerable progress.

Much of the past work on the structure of vulcanized rubber has been devoted to studying the kind of bonds formed when sulfur or sulfur chloride reacts with olefinic compounds. The following types of reactions occur with various unsaturated compounds and have been suggested as possible vulcanization reactions³²:



These reactions undoubtedly occur during hard rubber cures, but there is little evidence for them in the soft rubber range⁴⁰, aside from a few tests relating combined sulfur to loss of unsaturation in rubber-sulfur compounds, a few experiments on the evolution of hydrogen sulfide on heating rubber and sulfur, Meyer and

Hohenemser's identification²⁴ of C-S-C groups in cured rubber by their methyl iodide test, and a few others (including the work of Brown and Hauser described later).

Different compounds can be prepared with about the same physical state of cure but widely different amounts of combined sulfur¹⁶. It was once suggested⁸ that vulcanization with sulfur involves two reactions: One forms soft rubber with a heat of reaction that is very small or zero; the other, the ebonite reaction, evolves considerable heat. Later work showed that the heat evolution during sulfur cures is directly proportional to the combined sulfur, but with selenium or *m*-dinitrobenzene cures, there is no sensible evolution of heat.

All these polymerization or sulfur combination theories of vulcanization may be called "one-way" theories, since they try to account for the increase in tensile strength, etc., at the beginning of the cure, but they do not explain the decrease in some of these properties on overcures. Nor do they explain other facts such as the curious improvement in aging properties on long overcures of some low-sulfur stocks¹⁰, such as the improvement in aging of latex stocks by cure, although the cure may produce little change in the tensile properties, or such as the more common effects of overcures in decreasing the resistance to aging.

While these and many other theories were being proposed and discussed during the years since Weber's first work (1902), the technical compounder reduced the amount of sulfur in his compounds from around 10 per cent on the rubber to less than 3 per cent, and the number of essential curing ingredients in the compound has increased from one (sulfur) to four (sulfur+accelerator+zinc oxide+acid). When Bruni reported some years ago that he could detect measurable traces of vulcanization with as little as 0.15 per cent combined sulfur, it was a startling discovery. Today compounds are being made which contain a total of only 0.15 per cent available sulfur, yet give tightly cured, snappy stocks in less than 10 minutes at 300° F.

These practical developments have not led to corresponding advances in the theory of vulcanization. Rather, there has been too much of a tendency to force the facts to fit the old theories. The effect of accelerators, for example, is explained by assuming that they produce the active sulfur that presumably is needed for the postulated rubber-sulfur vulcanization reaction. The zinc oxide is assumed to work by activating the accelerator that activates the sulfur that then activates the rubber to form some postulated compound, and the stearic acid activates the zinc that activates the accelerator that, etc. Such Mother Goose rhymes may conceivably be true, but there is a much better chance that any one of these materials influences or reacts with the rubber more than it does with its next neighbor in this series. This possibility has been recognized in the literature^{24, 40}, but very little has been done to investigate it experimentally.

VULCANIZATION IN SOLUTION

The complexity of the sulfur chloride cure of cements is shown by the work of Garvey¹⁴, who found that the viscosity of 1.5 per cent cements of lightly milled rubber first decreased when they were treated with 10 per cent sulfur monochloride on the rubber, then increased until a gel was formed (within a few hours); but on standing overnight the gel liquified and produced a solution less viscous than the original cement. Under the same conditions corresponding cements of well-masticated rubber formed gels that were stable for at least a week. Mechanical agitation of the solution was found to prevent gel formation in some cases. On evaporation of some of the solutions that did not gel, solid films were

formed which were then insoluble in benzene. He suggests the possibility that gel formation is due in part to sulfur monochloride, which causes a geometric rearrangement (*cis-trans* isomerization) at some of the double bonds of the rubber, just as sulfur causes the isomerization of oleic to elaidic acid³². This would increase the kinkiness of the molecules and make it easier for them to interlock. On standing, some of this kinkiness might effectively be lost because rotation about some of the single valence bonds would cause the observed reversion.

It is also possible that there is some sort of dynamic equilibrium between the inter- and intramolecular bonds formed by the secondary valence forces around the polar (sulfur or chlorine) groups in these cured soft rubbers. If the initial conditions of concentration, etc., were just right, and the size or effective volume of the rubber molecules was not too great, it is conceivable that the combination with sulfur chloride should first produce intramolecular cross-bonds through the polar groups, which would tend to reduce the effective volume of the rubber molecules and the viscosity of the cement. It is known, for example, that the addition of a large amount of sulfur chloride to a dilute rubber cement causes the precipitation of the reaction product in the form of a powder, which shows that there has been a shrinkage of the rubber molecules and micelles. If the solution of the cured soft rubber were evaporated to obtain a solid film, there would then be a good chance for intermolecular bonds to form and thus make the evaporated film of rubber insoluble in hydrocarbon solvents. The addition of traces of polar materials might cause such films to dissolve if all the cross bonds were made through secondary valence forces.

If the rubber molecules were effectively very large and other conditions were right, it is possible that the opposite effect might occur—namely, that most of the initial cross bonds through valence forces were intermolecular, and that in the course of time many of them broke and were replaced by intramolecular bonds. This might explain the initial formation of gels in some of the cements of unmilled rubber, and their subsequent dispersion to yield solutions of low viscosity. However, in this case the possible effects of light and traces of acids in catalyzing the breaking of the chains cannot be overlooked.

Gehman and Field¹⁸ used the scattering and depolarization of light as well as viscosity tests to study the vulcanization of rubber in benzene in solutions, using sulfur, piperidinium pentamethylenedithiocarbamate (P. P. D.) and zinc propionate as curing agents. They conclude from light-scattering data that the size of the colloid units increases continuously from the time the curing ingredients are added, although they too found an initial drop in viscosity, followed by a later increase up to the stage of gel formation.

These facts show how difficult it is to interpret the effects of accelerators on rubber by means of viscosity tests. Not only can accelerators catalyze the breakdown of rubber by traces of oxygen present, but by purely physical means they may change the shape of the rubber molecules and thus change the viscosity without changing the molecular size.

If the curing time is defined as the time required for the original viscosity of the solution to be doubled, then with 2 per cent P. P. D. and 4 per cent sulfur, the curing time is a minimum with about 1 per cent zinc propionate. The curing rate decreases if more or less zinc propionate is used:

Zinc propionate (%)	Curing time (hours)
0.5	18
1	2.9
2	3.1
3	3.7
5	4.5

If the zinc content is low, a high P. P. D. concentration tends to retard the cure or gelation. They conclude that there is a reaction between the zinc salt and the P. P. D. rather than between the P. P. D. and the sulfur.

Williams⁴¹ found that the gelation time of cements of rubber, sulfur, zinc oxide and P. P. D. was increased by increasing the amount of P. P. D., and that an excess of P. P. D. made it possible to disperse a gel after it had formed. He found that the time required to disperse vulcanized rubber on immersion in various accelerators was greatly increased by the addition of soluble zinc salts.

In later work Williams⁴² peptized a number of rubber compounds in 5 per cent solutions of piperidine in toluene, fractionated the solutions, and analyzed the fractions for combined sulfur. The compounds included rubber 100, and the following: (a) sulfur 10 (2 cures); (b) sulfur 3, zinc oxide 2, butyraldehydebutylamine 0.5; and (c) sulfur 3, zinc oxide 2, and di-*o*-tolylguanidine 1.0. A compound (d) containing tetramethylthiuram disulfide 3 and no sulfur would not peptize. The solutions were fractionated by precipitation with alcohol, and the fractions analyzed for combined sulfur. Williams concludes that there is no direct relation between the physical properties of the rubber and either the amount of combined sulfur or the ease of peptization. The best vulcanized rubber appeared to be most heterogeneous with respect to combined sulfur, and high combined sulfur seemed to aid dispersion. The thiuram disulfide stock contained no free sulfur and did not disperse. On evaporation of the solutions of peptized rubber, films were formed "which had all the properties of vulcanized rubber", showing "that links by means of primary valence forces are not necessary for producing the vulcanized condition".

Many materials other than sulfur and accelerators stiffen rubber or make it unable to disperse in solvents, including organometallic compounds²⁸, benzidine and other aromatic diamines, magnesium oxide, carbon black (over 30 per cent on the rubber), nitroso- β -naphthol, nitrosobenzene, etc., benzoyl peroxides, etc., polynitrobenzenes, butyl nitrite, amyl nitrite, etc.

The wide variety of materials in this list suggests that cross bonds may be formed by widely different mechanisms. Organometallic compounds and benzidine are effective only with milled rubber, presumably because milling forms oxygen groups which react with these materials. The oxygen on the surface of carbon black may conceivably react with the rubber to form cross bonds. Intensive drying of rubber alone is enough to increase greatly the viscosity of its solutions, probably by the formation of cross bonds by the association of the polar (oxygen?) groups of different molecules. No good explanation has been offered for the fact that some nitroso compounds stiffen rubber while others are powerful softeners, or why basic oxides such as magnesia are powerful stiffeners.

The possibility that secondary valence forces may cause gel formation from solution cannot be ignored, since even low-molecular-weight crystalline materials may form gels on slow cooling of solutions in certain solvents. A new and striking example of this effect was discovered by Paul Jones of the B. F. Goodrich Company. He obtained clear solutions of fairly low viscosities by dissolving the sodium salt of di- β -naphthyl dithiocarbamate in hot alcohol or in hot water. When the alcohol solution cooled, the salt precipitated in the form of rather coarse crystals, but the water solution, on cooling, precipitated the salt in the form of a clear strong gel, even when the concentration was very low (2 to 5 per cent).

In the water solution the platelike naphthyl groups probably tend to pile together to expose as little hydrocarbon surface to the water as possible. If each naphthyl group of one molecule associates with a naphthyl group of a different

molecule, a chain structure will be formed. If naphthyl groups from three or more molecules pile together, branched chains can be formed that produce a gel structure. In the case of the corresponding diphenyl or phenyl- β -dithiocarbamates, the association forces probably are not strong or uniform enough to produce gels, and the compounds separate from water solutions as gelatinous precipitates. Further work on these systems should give some interesting information about the type of structure formed.

EFFECT OF INGREDIENTS ON CURE OF SOLID RUBBER

The literature is full of data which show the effects of various curing ingredients on physical properties of vulcanizates, but few if any attempts have been made to interpret these data in terms of the structural changes produced in the rubber by these ingredients. A few such data will be given here to show: (a) some of the phenomena that can be explained in terms of changes in molecular structures, and (b) more of the effects that cannot be explained by present theories of the vulcanization reactions.

A few generalizations may be noted which, though not universally valid, do hold for a rather wide range of high-gum compounds:

1. Low-sulfur compounds at optimum technical cure:

(a) Have a tendency to "freeze" or rack at relatively high temperatures, 0° C. (32° F.) or above.

(b) Show x-ray fiber diffraction patterns at relatively low elongation or at comparatively high temperatures.

(c) Have relatively high hysteresis with mechanical deformations.

(d) When stretched to moderate elongations, have a comparatively high rigidity towards shearing stresses in the "stretch and cut" test.

(e) Have less tendency to freeze after they have been through a bomb-aging test, even though the tensile properties have been almost unchanged.

These effects indicate that well-cured, low-sulfur stocks resemble to some extent unmasticated, uncured rubber. Evidently the cross bonds are not sufficiently numerous to interfere greatly with the crystallization of the rubber. In fact, the sharper x-ray diagrams obtained with cured low-sulfur stocks, compared to those of evaporated latex, for example, suggest that the cured rubber forms larger or more perfect fiber crystals than does the unmilled crude rubber. The high hysteresis of these compounds probably is due to the time lag of crystallization¹. Aging may have little effect on tensile properties, but it evidently interferes with the uniformity of the fibers enough to reduce the amount of crystallization and freezing.

2. High-sulfur accelerated stocks at overcures tend to:

(a) Have a low hysteresis.

(b) Be "heat brittle" and have a "brashy" or "brittle" hand tear.

(c) Have a low permanent set.

(d) Freeze or rack only at very low temperatures.

(e) Require higher elongations to give x-ray fiber diffraction patterns at room temperature.

(f) Have moduli at low (50 to 100 per cent) elongations which increase with increasing temperature, as predicted by thermo-dynamics.

These properties all suggest that the compounds have so many cross bonds or other nonuniformities along the fibers that they interfere with crystallization. However, many different types of reactions could produce these effects.

It should be mentioned that hard rubber is thermoplastic, suggesting that many of its cross bonds are due to secondary valence forces that can be broken by raising the temperature.

Simple tensile tests tell little about the type of structural changes involved, except perhaps as they show the effect of different ingredients on the over-all rate of cure. Tensile data³⁷ for compounds containing rubber 100 and sulfur 8, with and without zinc oxide 5, or with sulfur 3, zinc oxide 5, stearic acid 1, and mercaptobenzothiazole 1, show wide differences in rates of cure but only small differences in modulus, elongation and tensile strength at optimum cures.

A comparison of room temperature and high-temperature tensile tests sometimes gives more significant information about the type of bonds formed in different compounds, as Table I shows. All compounds contain rubber 100,

TABLE I
TENSILE PROPERTIES

Cure at 184° C. (278° F.) (min.)	Compound 1			Compound 2			Compound 3		
	Load at		Ultimate elongation (%)	Load at		Ultimate elongation (%)	Load at		Ultimate elongation (%)
	500% (lbs.)	Break (lbs.)		500% (lbs.)	Break (lbs.)		500% (lbs.)	Break (lbs.)	
AT ROOM TEMPERATURE									
15	465	2960	805	600	3420	760	290	2650	875
30	685	3250	730	550	3280	760	415	3110	805
45	795	3270	710	470	3220	780	430	3100	800
60	820	2980	695	465	3040	775	455	3150	780
90	820	2510	690	450	2830	785	475	3060	770
120	835	2110	660	395	2550	785	460	3090	775
150	760	1820	755	380	2350	800	470	3100	775
AT 100° C. (212° F.)									
15	360	3030	990	405	3710	1000	50	3350	1250
30	465	2720	920	410	3270	970	105	4010	1110
45	455	1420	785	310	2980	1000	130	4065	1090
60	490	535	520	280	2560	1000	155	4120	1075
90	—	240	425	250	2550	1010	145	3970	1065
120	—	205	350	235	2260	1060	145	4060	1050
150	—	180	310	210	2130	1050	140	3920	1065

stearic acid 1, zinc oxide 10, phenyl- β -naphthylamine 1, and accelerator and sulfur as follows:

Compound	1	2	3
Sulfur	3.5	1.5	0.4
Mercaptobenzothiazole	0.5	1.5	1
Tetramethylthiuram disulfide	—	—	0.3

The room-temperature tensile data for compound 1 show a slight increase in modulus with cure (to 120 minutes) and a gradual decrease in tensile strength and elongation; thus some reactions are occurring throughout the cure, but little evidence is given of what they are. At 100° C. the effects of overcure show up as a decrease in tensile strength from 3000 to less than 200 pounds, and in elongation a drop from 900 to 310 per cent.

A number of different explanations might be offered for this heat brittleness effect, such as breaking of association bonds at high temperatures, etc., but none

are entirely satisfactory. Probably the best explanation is that so many cross bonds are formed between the fibers, or that there are so many sulfur additions or cyclization reactions along the fibers, that the fibers cannot crystallize when stretched at the high temperature. The increased thermal vibration, combined with the decrease in entropy due to stretching, effectively produces a high internal pressure in the rubber and causes it to break at rather low elongations at the high temperature. This is consistent with the fact that such stocks must be cooled to relatively low temperatures to produce racking¹⁹.

As the sulfur is reduced in the above series of compounds, the tensile strength at optimum cure is not greatly changed, but the modulus is reduced and the elongation is increased. Even more important, these properties tend to become more nearly independent of cure, both at room temperature and at 100° C. It is remarkable that compound 3 has a lower modulus but a tensile strength nearly 1000 pounds greater and an elongation greater by nearly 300 per cent at 100° C. than at room temperature.

Many of the cross bonds formed in this low-sulfur stock evidently are stable to thermal vibration at 100° C. In fact thermal vibrations seem to lubricate the whole structure and make possible the internal rearrangements that produce the maximum tensile strength.

These properties, as well as Williams' work¹², tempt one to postulate that the bonds in the low-sulfur mercaptobenzothiazole-tetramethylthiuram disulfide stocks are principally at or near the ends of the rubber filaments, or at other specific points where they would be most effective. Possibly they are C-S-C bonds, but in view of the small amount of sulfur needed for some compounds, it is pos-

sible that some of these cross bonds may be $\begin{array}{c} | \\ \text{C}-\text{C} \\ | \end{array}$ or even C-O-C bonds.

Garvey^{15, 16} has given additional data to show how each of the various physical and chemical criteria of vulcanization might develop at a different rate in any one stock, and how the rates varied with the accelerator, sulfur concentration, etc. He concluded that there were at least two vulcanization reactions, one that involved sulfur and one that was merely catalyzed by sulfur.

In a study of reversion, Garvey showed that in stocks containing rubber 100, sulfur 0.5, zinc oxide 2.0 and accelerator 2.5, the amine (or basic) type of accelerators produced good tensile properties, but on long overcures the compounds would revert so badly that they resembled uncured rubber or reclaim. Sulfur-containing accelerators such as mercaptobenzothiazole, tetramethylthiuram monosulfide, tetramethylthiuram disulfide, etc., showed comparatively little reversion. Most of the stocks, except those with tetramethylthiuram monosulfide or tetramethylthiuram disulfide, could be reclaimed by milling on a hot mill. If the reclaimed stocks were then heated in a press without the addition of any more sulfur, those containing the sulphydryl type accelerators gave distinct evidence of further cure, but no cure was obtained on heating the reclaimed stocks containing amine accelerators. Much more work will have to be done to unravel the structural changes producing these effects.

The problem of the effect of accelerators on the structure of cured rubber is closely connected with the effect of zinc oxide or other oxides on the structure, for very few accelerators are active in the absence of zinc oxide or some other metallic oxide⁹. The addition of zinc oxide to a rubber-sulfur stock increases the rate of cure, it has been claimed²⁷, "because it activates the natural accelerator in the rubber". The addition of 20 parts zinc laurate to a normal mercaptobenzo-

thiazole-hexamethylenetetramine stock greatly increases the modulus; this suggests that it forms more cross bonds.

From a stock having rubber 100, sulfur 3, and mercaptobenzothiazole 0.5, cured with and without 5 parts of zinc oxide, the data given in Table II were obtained.

The compound with zinc oxide gave normal cures, the overcures being rather brittle at high temperatures. Without any zinc oxide the tensile properties were very poor and the hand tear felt rather brittle and "glassy", but the torn surfaces were tacky. This and the 100° C. tensile tests make the stock without zinc oxide seem uncured.

The effect of the zinc oxide cannot be mainly to form the zinc salt of mercaptobenzothiazole, for if this compound is used in the absence of added zinc oxide the cures are not much better than when mercaptobenzothiazole alone is used. Even the addition of a zinc soap to the compound is not as effective as the addition of zinc oxide.

TABLE II
PHYSICAL PROPERTIES

Cure at 160° C. (320° F.) (min.)	With ZnO			Without ZnO		
	Load at		Elonga- tion (%)	Load at		Elonga- tion (%)
	600% (lbs.)	Break (lbs.)		600% (lbs.)	Break (lbs.)	
AT ROOM TEMPERATURE						
10	560	3020	870	260	500	1180
30	450	2500	890	190	900	1090
120	320	2200	950	125	650	1150
AT 100° C. (212° F.)						
10	550	2500	900	110	180	890
30	—	390	330	175	160	765
120	310	445	750	150	230	775

A number of other physical tests may give considerable information about the structure of rubber. The difference between the stress-strain curve on extension and on retraction may give some measure of the number of "loose ends" of fibers within the meshes of the three-dimensional network structure. If a compound shows a nearly reversible stress-strain curve on extension and retraction, this is evidence that the whole structure is tied together in the three-dimensional network. Such a compound would also have very low creep. Rapid cyclic hysteresis tests, as well as long-time creep tests give physical results which are determined by, and some day perhaps can be interpreted in terms of, the molecular structures.

X-rays, tear tests and racking give some evidence of the uniformity of the fibers and their tendency to crystallize on stretching⁶. An intensive study of the effect of diluents such as oil on these properties might furnish a means of studying the general building plan of the molecular networks.

An important contribution to the study of the chemistry of vulcanization was made recently by Brown and Hauser⁴ when they determined the ratio of the loss of unsaturation to the combined sulfur in a number of technically important accelerated stocks over a wide range of cure. With any particular accelerator, the ratio was about constant during the initial stages of the cure, but the unsaturation often continued to decrease during overcures after most of the sulfur had combined,

probably due to some sort of polymerization or cyclization of the molecules under the influence of heat and accelerators.

A stock containing rubber 100 and sulfur 8 acquired one atom of combined sulfur per double bond lost, up to about 5.5 per cent combined sulfur or for cures up to and slightly past the optimum tensile cure. If 5 per cent zinc oxide was added to this stock, then at the lower cures nearly two atoms of sulfur were combined per double bond lost. Compounds containing rubber 100, stearic acid 0.5, zinc oxide 5.0, and sulfur 2.5, and accelerated with either tetramethylthiuram monosulfide 0.25 or mercaptobenzothiazole 0.5, had nearly two atoms of combined sulfur per double bond lost up to the optimum tensile cure. Similar compounds accelerated with zinc dimethyldithiocarbamate or heptaldehydeaniline gave values between 1 and 2 for this ratio. Attempts to identify and determine quantitatively the exact types of bonds formed were not successful; even the methyl iodide test for thioether linkages were somewhat inconclusive.

It is important that these data be confirmed and extended but, even as they stand, they show the complexity of the vulcanization processes, the need for more accurate and specific physical and chemical tests for the reactions involved and the necessity of detailed studies of a wide range of compounds having various types of accelerators and cured under different conditions. To carry out such a complete series of tests would not only be very difficult but also time-consuming and expensive. However, the results should more than repay the cost by reducing the amount of expensive empirical testing now required to develop and evaluate new compounds and new accelerators. The results may also help to produce a rubber having some of the desirable properties found in synthetics.

The solution of the problem will require extensive work on (1) more sensitive chemical tests for the possible chemical reactions and applications of these tests to a wide variety of compounds, and (2) physical tests for change in structure, including low and high temperature tests for tensile strength, permanent set, and tear and measurements of x-ray fiber diffraction patterns, thermodynamic properties, etc.

The tests must be interpreted in light of the vast store of practical information available in the rubber industry, but the problem is too big for any one company to hope to solve in a reasonable time, and too important for any large company to ignore.

If we want to have some of the answers to this problem before the next centennial of Charles Goodyear's great discovery, and if we want the answers at the lowest cost, it will be wise to make this the major problem of a cooperative research program by the rubber industry¹⁷.

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EFFECT OF RUBBER VARIABILITY ON VULCANIZATION *

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When Charles Goodyear was carrying out his early experiments in 1839 with the process subsequently described as vulcanization, he could scarcely have realized in the wildest flights of imagination how vast and widespread the rubber industry was to become. To him one sample of wild rubber must have appeared similar to another and he would have found it difficult to believe that one day millions of acres of *Hevea brasiliensis* in the East would be supplying almost exclusively the raw rubber needs of the world. With the growth of this vast industry have come inevitable problems which the consumer has to face; not the least of them is the variation in behavior of plantation raw rubber on vulcanization.

Since 1910 when plantation rubber first began to appear in quantity, the consumer has found difficulty in handling different consignments and has constantly complained of its variable vulcanizing properties. At the Fourth International Rubber Conference held in London in 1914, Williams¹² appealed for efforts to be made by the plantations to produce a more uniform rubber, and stated that the "average plantation rubber as turned out today is not equal to Para in uniformity or strength. In Para the washing loss is practically constant. Vulcanization does not present any material difficulties to the manufacturer. The same can not be said of plantation rubber".

At that time the plantation industry was producing approximately 45 per cent of the world's total; in 1938 it produced nearly 97 per cent of a total which was more than seven times that of 1913. Although plantation rubber has almost entirely replaced Para, Williams' observations on the difficulties caused by the variability of its vulcanizing properties are equally applicable today. Twenty-four years later at the Rubber Technology Conference in London, Heywood⁷ described experiments indicating difficulties which variation can cause the consumer; he concludes: "It seems clear that this series of experiments has proved that the variation which is apparent in raw rubber is still apparent in the finished tyre. . . . One can easily see from the results obtained the necessity for testing all rubbers received and of blending to obtain a uniform raw rubber with which to commence compounding."

In view of these statements it might appear that little progress has been made during the last twenty-four years toward the fulfillment of consumers' wishes. Although uniform raw rubber is unfortunately not readily available, the plantation industry has not been indifferent to the consumers' requirements. From the earliest days continual and patient research work has been carried out by scientists working on behalf of the producers to investigate the underlying causes of variation in the vulcanizing properties of plantation rubber. As a result of this work, which has been carried out mainly in the producing countries, a great deal of information has been gathered on the problem, and improvements in the methods of preparation have taken place.

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Deliberate alteration in the methods of preparation of plantation rubber will usually react on the vulcanizing properties. A fairly complete understanding of the influence of the treatments used in the preparation of the usual types of rubber (sheet and crepe) has been obtained by the researches of Eaton and his co-workers in the Malaya^{4, 5, 6} and by de Vries and his collaborators in Java¹¹. It is largely as a result of their work that the methods of preparation now used on the plantations are more closely controlled than in the early days.

The work carried out by these investigators also indicated that variability was not caused entirely by methods of preparation and that inherent differences in the latex played a part; variation should be considered, therefore, as arising from both controllable and uncontrollable causes. Controllable causes depend almost entirely on estate factory procedure; uncontrollable causes are natural factors such as genetic strain, age and condition of the trees from which the latex is obtained, types of soil and climatic and seasonal changes. Tapping systems and methods of soil treatment, notably manuring, are also not entirely controllable, since they often depend on market and other economic considerations.

In this paper it is proposed to confine attention to the effect of variation in vulcanizing properties of No. 1 sheet because it is in this form that the consumer uses the major part of his requirements and, moreover, variability in first quality crepe is less than in sheet.

EXTENT OF VARIABILITY

In 1924 the Dutch workers in Java adopted a standard of normality for the vulcanizing properties of raw rubber. A sample was defined as normal if the time of vulcanization required to reach a fixed state of cure in a rubber-sulfur mix was within ± 20 per cent of the average, and defined as uniform if within ± 10 per cent. During the period 1921-23 de Vries tested many estate samples of sheet and reported¹⁰ that 60 per cent were uniform and 90 per cent normal; in 1929 Riebl⁸ found from an examination of a number of samples of smoked sheet received from various estates in Java that 87 per cent were uniform and 90 per cent normal. In 1927 Eaton and Bishop³ and in 1932 Bishop and Fullerton¹ examined samples of estate smoked sheet and concluded that there was a high degree of variation in the vulcanizing properties. In the above investigations a simple rubber-sulfur mix was used with which to compare the vulcanizing properties, although work with this type of mix has been criticized on the grounds that it is not used in practice and conclusions drawn from its use are not necessarily the same as those obtained in an accelerator mix.

The rubber producers' research organizations continue to work on this problem of variability, and an investigation has recently been carried out at the Rubber Research Institute of Malaya to obtain information on the extent of variation which still occurs in plantation rubber. Smoked sheet was obtained from 157 European-owned plantations in various parts of the country in response to a request for samples of their standard No. 1 product. All rubbers were prepared on or about the same day, and seasonal effects were thereby eliminated as far as possible. Table I gives the distribution of the estates, their acreage, and the percentage of the total planted estate acreage of Malaya; thus the samples examined were from widely distributed estates comprising a fifth of the total acreage and can be regarded as reasonably representative of No. 1 sheet now being produced by Malayan plantations.

The samples were mixed in a rubber-sulfur (100-10) mix and cured for 120 minutes at 148° C. in an open steam vulcanizer, and rings were pulled on the

TABLE I
DISTRIBUTION OF ESTATES

State	Total planted acreage *	Estates participating in examination		
		No.	Planted acreage	% of total planted
Federated Malay States:				
Perak	307,345	16	30,265	10
Selangor	351,841	27	45,374	28
Negri Sembilan	283,102	27	72,138	26
Pahang	91,138	12	22,986	25
Straits Settlements:				
Singapore, Malacca, Penang...	207,790	7	28,700	20
Unfederated Malay States:				
Johore	523,145	39	122,412	23
Kedah	208,652	29	82,894	35
Kelantan	32,542	—	—	—
Perlis	1,674	—	—	—
Trengganu	13,153	—	—	—
Brunei	5,966	—	—	—
Total	2,026,348	157	404,769	20

* Does not include small holdings.

Schopper tensile strength tester. The usual 24-hour cycle between mixing, curing, and testing was observed. As a result of the excellent work of the Crude Rubber Committee of the American Chemical Society, a standard formula for an accelerator mix has been evolved and is now widely adopted. In addition to the rubber-sulfur mix this standard mercaptobenzothiazole mix was used in the examination of the samples:

Rubber	100
Sulfur	3.5
Zinc oxide	6.0
Stearic acid	0.5
Mercaptobenzothiazole	0.5

Mixes were cured for 40, 60, 80 and 100 minutes at 127° C. and rings were pulled on the Schopper tester. For the purpose of this paper it is not necessary to give complete modulus and tensile figures, and Table II shows the distribution of the samples classified according to the modulus figures taken at 800 per cent for the rubber-sulfur cures and at 700 per cent elongation for the 60-minute mercaptobenzothiazole cures.

These results indicate that there is considerable variation in the vulcanizing properties of the samples, and this is more readily seen from the distribution histograms of Figure 1.

COMPARISON OF RUBBER-SULFUR AND MERCAPTOBENZOTHAZOLE MIXES

At first it appears that the rubbers are considerably more variable in the rubber-sulfur than in the mercaptobenzothiazole mix; but this is not necessarily the case, as consideration of the interpretation which must be given to the modulus figures in the rubber-sulfur mix will show. The usual method of reporting vulcanization results in this type of mix is in terms of time of vulcanization required to reach maximum tensile strength, but unfortunately the time and number of

TABLE II

DISTRIBUTION OF MODULI^a IN MERCAPTOBENZOTHAZOLE AND RUBBER-SULFUR MIXES

Mercaptobenzothiazole			Rubber-sulfur		
Modulus at 700% elongation (kg./sq. mm.)	No. of estates	% of total number	Modulus at 800% elongation (kg./sq. mm.)	No. of estates	% of total number
0.39 or less	20	13	0.39 or less	13	8
0.40-0.49	59	60	0.40-0.49	25	60
0.50-0.59	36		0.50-0.59	44	
0.60-0.69	29		0.60-0.69	25	
0.70-0.79	9	27	0.70-0.79	15	
0.80-0.89	1		0.80-0.89	8	32
0.90-0.99	3		0.90-0.99	5	
			1.00-1.09	4	
			1.10-1.19	7	
			1.20-1.29	4	
			1.30-1.39	2	
			1.40-1.49	4	
			1.50	1	

^a Mean modulus for all samples: Mercaptobenzothiazole = 0.52 and rubber-sulfur = 0.67 kg. per sq. mm.

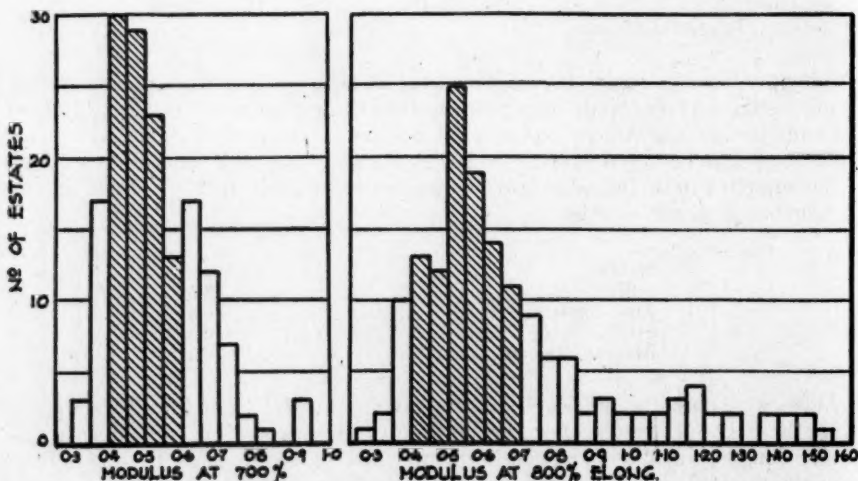


Fig. 1.—Modulus distribution.

observations involved in the examination of these samples have made it impossible to report the variation in this manner at present. However, as Wiltshire¹⁸ points out, determination of tensile modulus at a fixed elongation and time of cure permits comparison within a series of samples and enables a prediction of the time of cure necessary for maximum tensile strength to be made with reasonable accuracy. This can be done, however, only when the relation between time of cure and modulus has been well established for the methods of testing used in a particular laboratory. Moreover, the straight-line relation between modulus and time of cure which is evident over a fairly wide range does not hold when the modulus is high. Data on the relation between the time of cure and the range of modulus which occurs among these samples were not available in this laboratory, and it was not possible to predict and report the time of cure of all samples from the modulus figures. It is therefore likely that the range of moduli shown

in Figure 1 indicates a greater variation among the samples, particularly among the faster curing samples, than would be indicated by a time-of-cure distribution. Sixty per cent of the rubbers have modulus figures at 800 per cent elongation which lie between 0.40 and 0.69 kg. per sq. mm., inclusive, in the rubber-sulfur mix. These modulus figures correspond to approximately 135 and 165 minutes of cure, for which region the straight-line relation is applicable.

In view of the criticisms which have been made from time to time against the use of the rubber-sulfur mix, it is of particular interest to compare the result of testing these estate rubbers in the mercaptobenzothiazole and rubber-sulfur formulas. Table II indicates that twenty samples tested in the mercaptobenzothiazole stock had moduli less than 0.40 kg. per sq. mm., 95 between 0.40 and 0.59, inclusive, and 42 greater than 0.59; in rubber-sulfur 13 were less than 0.40 kg. per sq. mm., 94 between 0.40 and 0.69, and 50 greater than 0.69. The inclusive modulus ranges 0.40-0.59 and 0.40-0.69 kg. per sq. mm. for the mercaptobenzothiazole and rubber-sulfur mixes, containing ninety-five and ninety-four estates, respectively, are marked in the histograms of Figure 1 by shading; as mentioned above they account for 60 per cent of the total number of estates. The results of the tests of the individual samples in both mixes were therefore

TABLE III
COMPARISON OF RUBBER-SULFUR AND MERCAPTOBENZOTHIAZOLE MIXES

Rubber-sulfur		Mercaptobenzothiazole			
		Modulus class			No. of estates
Modulus class (kg./sq. mm.)	No. of estates	Lower, 0.40 (kg./sq. mm.)	Middle, 0.40-0.59 (kg./sq. mm.)	Higher, 0.59 (kg./sq. mm.)	
Lower, 0.40	13	10	3	—	13
Middle, 0.40-0.69	94	10	78	6	94
Higher, 0.69	50	—	14	36	50
	157	20	95	42	157

compared in order to see if those in the lower, middle, and higher classes when tested in the mercaptobenzothiazole mix were in similar grades in the rubber-sulfur classification. The results are shown in Table III and indicate good correlation. In no instance has a sample found to be in the lower or higher class when tested in rubber-sulfur appeared in the reverse order in the mercaptobenzothiazole mix; although the correlation is not perfect, it would appear that the information obtained by the use of a pure gum mix is not in conflict with that given by the accelerator type.

REDUCTION OF VARIABILITY BY BLENDING

The consumer frequently has to contend with variation similar to that described above, and he attempts to achieve uniformity for the vulcanizing processes by blending rubbers from various consignments before compounding. It is therefore interesting to obtain from the data an estimate of the number of samples taken at random from among those tested which would be required for blending, in equal proportions, in order to obtain reasonable likelihood (95 per cent probability) that the vulcanizing properties of the blend would fall within a specified range. An attempt has been made to do this from the modulus results in the mercaptobenzothiazole mix. The shaded part of the histogram (Figure 1),

in which lie 60 per cent of the samples with moduli between 0.4 and 0.59 kg. per sq. mm., was selected for the specified range. It has been assumed that the modulus of a mixture of equal amounts of different samples will be equal to the mean of the moduli of the individual samples; this assumption is approximately true in mercaptobenzothiazole mixes. The distribution of moduli of single samples is skew (Figure 1); but if the number blended is sufficiently large, the mean modulus will tend to be distributed normally, and calculations based on normal statistical theory may serve to estimate a first approximation to the number of samples required. With a mean at 0.52, 95 per cent of normally distributed variates will fall in the range 0.40 to 0.59, the specified limits, when the standard deviation is 4.23. Since the standard deviation of the mercaptobenzothiazole moduli for individual samples is 12.27, the number which would need to be blended to give a mean modulus with a standard deviation of 4.23 is $(12.27/4.23)^2$ or 8.4.

CONTROLLABLE VARIATION

The researches of the earlier workers on the causes of variability have shown that the rate of vulcanization will be affected by changes in the process of manufacture which will alter the ratio of certain nonrubber substances to rubber present in the final product. Part of the nonrubber substances are present in the serum of the latex, and any variation in the method of manufacture which affects the amount present in the sheet will almost certainly produce a corresponding effect on the vulcanizing properties. In the early days of the plantation industry, methods of manufacture varied considerably; and in spite of the continued efforts of the research organizations in the East to achieve uniformity by advising a standard procedure, variation still exists although it is now much less than before. The following brief consideration of some of the stages in the preparation of sheet rubber will indicate that, although they do have an effect on the general problem of variability, it is not so great as might be supposed.

De Vries' investigations¹¹ indicated that the composition of the latex may have a marked effect; for example, rubbers from trees of different ages behave differently on vulcanization, and he indicated the necessity of minimizing these effects as far as possible by mixing the latex before manufacture. This has been recognized by the plantations, and the majority today have facilities for bulking a large proportion, if not all, of their crop. But as Sackett⁹ showed, there appears to be a reasonable limit to the size of the bulking used, beyond which no improvement in uniformity is obtained.

Under the present marketing system, the producer is usually compelled to pay particular attention to the appearance of his sheet to obtain full market price. On many estates, particularly at certain times of the year, an anticoagulant must be used in the field or the factory in order that sheet of finer appearance can be produced. Several chemicals have been employed for this purpose, but only sodium sulfite and ammonia are now generally used on the plantations in Malaya. Sodium sulfite has a slight accelerating effect; and according to more recent work with accelerator mixes, ammonia was found by Sackett⁹ to accelerate the rate of vulcanization and by Bocquet² to retard it when used in quantities requiring extra acid for coagulation.

The nature of the coagulant and the amount used affect the vulcanizing properties in a rubber-sulfur mix; the following comparison of tests in mercaptobenzothiazole and rubber-sulfur mixes indicates the influence of excessive amounts of coagulant. A series of smoked sheets was prepared from a single bulk of latex

by coagulating with formic, acetic and sulfuric acids; amounts normally recommended and multiples of these quantities were used. The sheets were given identical preparation treatment, and when dry were vulcanized in mercaptobenzothiazole and rubber-sulfur mixes for 60 and 120 minutes at 127° and 148° C., respectively. The results (Table IV) indicate that increased amounts of acid generally cause retardation but also that the use of acid in an amount far in excess of that normally required does not produce a large variation. The rubber-sulfur mixing shows the well-known retarding influence of sulfuric acid which is not, however, shown in the mercaptobenzothiazole mix. Malayan producers have been advised not to use sulfuric acid as a coagulant¹⁴, and a recent questionnaire indicated that considerable uniformity existed among estates; approximately 90 per cent are now using formic acid.

The variation which may arise from indifferent amounts of rolling and washing of the coagulum, particularly the rolling, and from different draining and drying treatments of the wet sheet, is likely to be greater than that caused by a variation in the amount of acid used for coagulation, because these processes still vary considerably among estates. Eaton and de Vries showed that the dilution at which the latex is coagulated has an effect on the vulcanization properties in a rubber-sulfur mix and Sackett has confirmed their findings in a mercaptobenzothiazole mix. But dilution has little effect in modern estate practice because the producer is compelled to keep within fairly narrow limits in order to produce sheet of good appearance; and if the subsequent rolling of the coagulum and drying of the sheet were more uniform among estates, it is doubtful whether it would markedly influence variability.

The amount of washing which the coagulum is given during the rolling process and subsequent soaking of the wet sheet have also been found by the earlier workers to affect vulcanization; this might be expected from the generalization that any treatment which tends to alter the ratio of nonrubber substances to rubber is likely to alter the rate of vulcanization. Very few estates preparing sheet rubber in Malaya today soak their wet sheet; but many have a poor water supply, and it is of interest to ascertain how much variation this would produce. Table V gives the results of vulcanizing sheets prepared from a single bulk of latex by identical treatment except for the amount of washing and soaking the coagulum has received during and after rolling. Drying was carried out in a smokehouse at 125-135° F. (51.7-57.2° C.) and in a hot-air cupboard thermostatically maintained at 140° F. (60° C.). The modulus figures indicate a slight retardation owing to the soaking of the wet sheet, but the amount of water used during the sheeting process does not appear to have affected the vulcanizing properties.

The conditions of drying also have an influence and, in general, smoking has a tendency to retard the rate of cure; however, different investigators have found widely divergent results attributable to smoking, and de Vries remarked¹¹ that more work is required before the effect of smoking on rate of curing is understood in all its details. Investigations, of which the results will be published shortly, have been in progress at the Rubber Research Institute on the effect of drying conditions on the vulcanizing and aging properties of sheet rubber. They indicate that this stage of preparation is important and undoubtedly contributes towards variability. The temperature at which the drying is carried out appears to have a slight but noticeable effect on the rate of curing, even when the drying is rapid, whereas the degree of smoking which the sheet receives also has an appreciable effect. The results shown in Table VI are indicative

TABLE IV
EFFECT OF COAGULANT AND AMOUNT USED ON THE VULCANIZING PROPERTIES OF SMOKED SHEET

	Amount of coagulant	Modulus *			Tensile strength (kg./sq. mm.)			% Elongation at break		
		Formic acid	Acetic acid	Sulfuric acid	Formic acid	Acetic acid	Sulfuric acid	Formic acid	Acetic acid	Sulfuric acid
Mix Mercaptobenzothiazole	Normal	0.52	0.51	0.57	1.39	1.38	1.74	903	900	920
	2 X normal	0.47	0.49	0.57	1.25	1.31	1.51	898	900	899
	4 X normal	0.43	0.47	0.53	1.29	1.24	1.39	919	908	896
	6 X normal	0.66	0.49	—	1.69	1.34	—	883	906	—
Rubber-sulfur	Normal	0.65	0.66	0.45	1.39	1.40	1.27	942	940	982
	2 X normal	0.50	0.57	0.27	1.35	1.24	0.95	977	946	1034
	4 X normal	0.44	0.51	0.22	1.20	1.25	0.79	985	973	1053
	6 X normal	0.67	0.48	—	1.39	1.20	—	924	974	—

* In mercaptobenzothiazole at 700%; in rubber-sulfur at 800% elongation.

TABLE V
EFFECT ON VULCANIZING PROPERTIES OF WASHING DURING PREPARATION

	Drying treatment of wet sheet		700% Tensile modulus strength		800% Tensile modulus strength		Elongation (%)
	Hot air or smoke	Temp. (° F.)	Time (Days)	(kg. per sq. mm.)	(kg. per sq. mm.)	(kg. per sq. mm.)	
Washing treatment of coagulum							
No water on machines, no soaking	Smoke	125-135	4	0.41	1.28	0.44	927
Full water on machines, no soaking				0.42	1.26	0.46	916
Full water on machines, 2-hrs. soaking in running water				0.35	1.01	0.41	911
No water on machines, no soaking	Hot air	140	3	0.43	1.31	0.62	905
Full water on machines, no soaking				0.43	1.35	0.62	917
Full water on machines, 2-hrs. soaking in running water				0.35	1.14	0.53	929
Full water on machines, no soaking	Hot air	140	4	0.44	1.40	0.67	920
Same			5	0.43	1.35	0.66	916
						1.21	986
						1.33	1000
						1.05	977
						1.42	953
						1.46	955
						1.40	979
						1.44	943
						1.39	937

of the effect which the conditions of drying of the wet sheet may have on the vulcanizing properties of the dry rubber. A series of sheets was prepared from a single bulk of latex by identical treatment up to the drying stage, and they were then taken to various estates near the Rubber Research Institute and dried together with the estates' standard sheet. The time required to complete the drying varied in the different smokehouses, but there is no apparent correlation between the period of drying and the vulcanizing properties.

The results of these experiments, in conjunction with other work, seem to show that the variation in present-day methods of preparing sheet is not responsible for as much of the variability as is usually attributed to it. Nearly twenty years ago de Vries found that rubber prepared in an identical manner on different estates appeared to exhibit as wide a variation in vulcanizing properties as that normally found in estate rubber, and his conclusion is interesting:

TABLE VI
EFFECT OF DRYING CONDITIONS ON VULCANIZING PROPERTIES

Where dried Rubber Research Inst.:	Mercaptobenzothiazole			Rubber-sulfur		
	700% modulus	Tensile strength	Elon- gation	800% modulus	Tensile strength	Elon- gation
	(kg. per sq. mm.)		(%)	(kg. per sq. mm.)		(%)
In hot air.....	0.45	1.42	923	0.81	1.46	914
In smoke.....	0.30	1.08	974	0.39	0.99	981
Smokehouse:						
Estate A.....	0.56	1.52	989	0.86	1.46	905
Estate B.....	0.54	1.53	909	0.83	1.61	928
Estate C.....	0.54	1.51	908	0.84	1.59	924
Estate D.....	0.41	1.30	929	0.45	1.31	998
Estate E.....	0.35	1.04	922	0.39	1.05	995
Estate F.....	0.58	1.55	891	1.21	1.31	828
Estate G.....	0.47	1.32	905	0.57	1.38	960
Estate H.....	0.39	1.34	945	0.55	1.42	972
Estate I.....	0.39	1.30	932	0.49	1.38	986
Estate J.....	0.38	1.41	917	0.49	1.35	988

"The 'composition of the latex' therefore may cause as great a variation in the rubber as the preparation if not a greater one; and in proportion as the preparation on estates becomes more and more standardized, variation in the latex will be of more and more importance as a cause of variability in the product, because they depend on the condition and treatment of the plantation, which cannot always be regulated at will."

UNCONTROLLABLE VARIATION

Space does not permit a detailed discussion of the effect of uncontrollable influences, but the results of an experiment now in progress in Malaya on the effect of the tapping system fully support de Vries' statement. A field of normal, well-grown seedling trees at the experiment station of the Rubber Research Institute was used; the trees were 6 years old when tapping commenced. The field was divided into six full tasks, with two tasks of each of the following tapping systems: alternate daily tapping on single half-cut spiral, continuous tapping; daily tapping on single half-cut spiral, alternate monthly tapping; Sunderland system, third daily tapping on two half-cut spirals, 6-month tapping, 6-month

TABLE VII
EFFECT OF TAPPING SYSTEM ON VULCANIZATION

Month	Task 1 *		Task 2 *		Task 3 *		Task 4 *		Task 5 *		Task 6 *	
	Mercaptoben- zothiazole, 700%	Rubber- sulfur, 800%	Mercaptoben- zothiazole, 700%	Rubber- sulfur, 800%	Mercaptoben- zothiazole, 700%	Rubber- sulfur, 800%	Mercaptoben- zothiazole, 700%	Rubber- sulfur, 800%	Mercaptoben- zothiazole, 700%	Rubber- sulfur, 800%	Mercaptoben- zothiazole, 700%	Rubber- sulfur, 800%
	Modulus in kilograms per square millimeter											
Oct., 1936.....	0.64	0.58	—	—	0.66	0.64	0.59	0.51	—	0.79	0.57	0.45
Nov.	0.80	0.87	—	—	0.76	0.81	0.72	0.70	—	0.67	—	—
Dec.	0.90	1.05	—	—	0.75	0.79	0.84	1.02	—	—	0.72	0.63
Jan., 1937.....	0.89	0.93	—	—	0.77	0.76	0.84	0.90	—	0.78	—	—
Feb.	0.84	0.93	—	—	0.76	0.84	0.79	0.94	—	—	0.71	0.74
March	0.71	0.62	—	—	0.72	0.81	0.77	0.79	—	0.65	—	—
April	—	—	0.51	0.48	0.75	0.82	0.76	0.81	—	0.70	0.71	0.68
May	—	—	0.80	1.06	0.74	0.84	0.88	1.13	—	0.74	0.86	—
June	—	—	0.70	0.84	—	—	0.82	1.14	—	—	0.76	0.84
July	—	—	0.66	0.78	—	0.88	0.86	1.10	—	0.72	—	—
Aug.	—	—	0.65	0.73	0.75	0.81	0.84	1.21	—	0.81	0.73	0.83
Sept.	—	—	0.75	0.94	0.75	0.81	0.79	1.02	—	0.69	0.67	0.69
Oct.	0.40	0.36	—	—	0.81	0.97	0.80	0.99	—	—	0.57	—
Nov.	0.65	0.59	—	—	0.80	0.84	0.78	0.88	—	0.66	—	—
Dec.	0.65	0.70	—	—	0.83	0.90	0.74	0.73	—	—	0.76	0.79
Jan., 1938.....	0.70	0.91	—	—	0.78	0.92	0.80	1.05	—	0.73	—	—
Feb.	0.63	0.78	—	—	0.82	1.07	0.73	1.01	—	0.63	0.65	0.78
March	0.60	0.66	—	—	0.77	0.86	0.69	0.81	—	0.75	—	—
April	—	—	0.41	0.41	0.67	0.67	0.61	0.64	—	—	0.57	0.60
May	—	—	0.56	0.64	0.62	0.62	0.62	0.71	—	0.59	—	—
June	—	—	0.56	0.68	0.58	0.67	0.59	0.70	—	—	0.56	0.60
July	—	—	0.51	0.60	0.66	0.73	0.62	0.73	—	0.67	—	—
Aug.	—	—	0.49	0.54	0.64	0.67	0.59	0.67	—	—	0.57	0.63
Sept.	—	—	0.62	0.83	0.71	0.97	0.63	0.87	—	0.63	—	—
Oct.	0.32	0.25	—	—	0.67	0.77	0.67	0.75	—	0.82	0.61	0.56
Nov.	0.53	0.46	—	—	0.64	0.57	0.63	0.60	—	0.56	0.51	—
Dec.	0.58	0.56	—	—	0.64	0.68	0.60	0.59	—	—	0.58	0.59

* Two half-cut spirals, third daily tapping, 6 months' tapping, 6 months' resting.

* Single half-cut spiral, alternate daily continuous tapping.

* Single half-cut spiral, daily tapping, 1 month's tapping, 1 month's resting.

resting. The tasks were so arranged that when one Sunderland task was in tapping, the other was resting, and similarly for the daily alternate monthly tasks. The trees were opened up as in normal estate practice, and from the commencement of tapping the latex has been made into smoke sheet by a rigidly

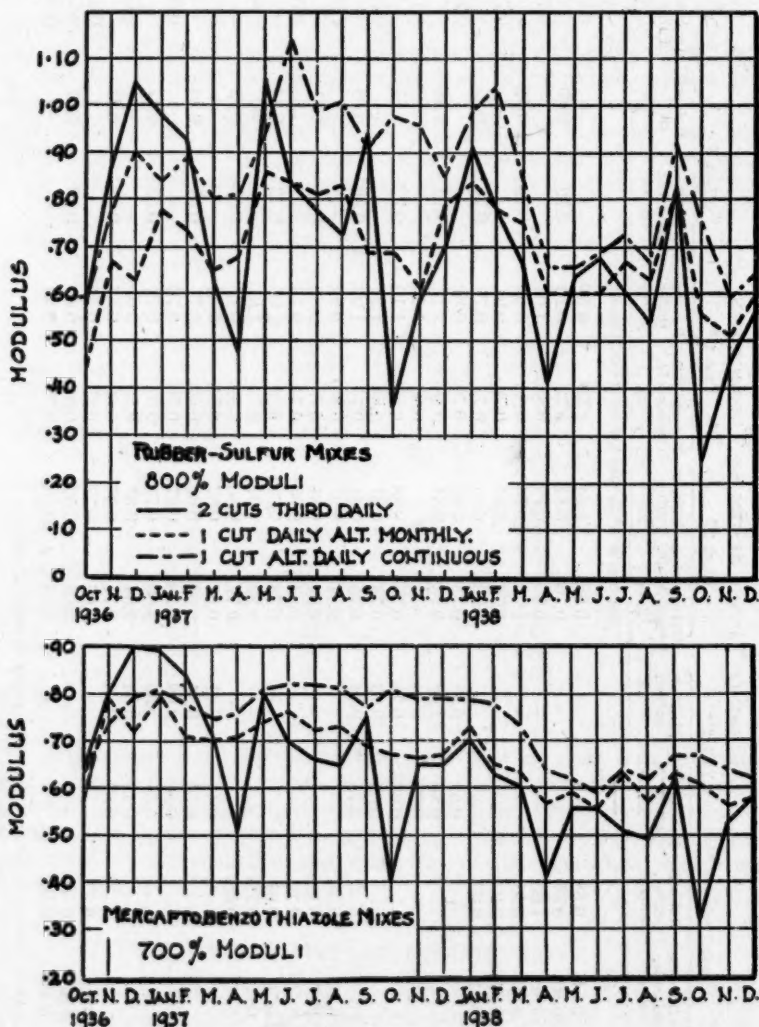


FIG. 2.—Effect of tapping system on vulcanization.

controlled and standardized preparation procedure. As far as possible all steps have been taken to prevent variation owing to conditions of preparation. The experiment has been proceeding since September, 1936, and the results of vulcanizing samples in mercaptobenzothiazole and rubber-sulfur mixes representative of all sheet prepared from each task every month are shown in Table VII.

The modulus figures for the 60-minute cure in the mercaptobenzothiazole formula only are given, together with those for the 120-minute cure in the rubber-sulfur mix. Tasks 3 and 4, which are both on the alternate daily system, show appreciable differences in the first year of tapping, after which the results are substantially the same. In Figure 2, where the effect of the three systems is more readily seen, the mean modulus figures for tasks 3 and 4 are used.

The results of the tests in the rubber-sulfur are paralleled in the mercaptobenzothiazole mix and clearly indicate the Sunderland system of tapping to be the least desirable when judged by the effect on variability. There is a noticeable retardation in the rate of vulcanization as the age of the trees increases, and this is particularly evident in the Sunderland system. In each of the 6-month periods of tapping in task 1 the modulus rises to a maximum and then falls before resting begins; task 2 behaves similarly except that in both periods of tapping, April to September, 1937 and 1938, there is a pronounced rise in September just before tapping ceases. Whether this is a seasonal variation or a peculiarity of the plot is not yet known, although no indications of seasonal variation are apparent in the results of the other systems. This experiment will continue over a long period and in due course will provide valuable information on the effect on variability of the age of trees, height of tapping cut, change in tapping and other factors.

CONCLUSIONS

It is hoped that the results given will have indicated that the effect of variation on vulcanizing properties is well recognized by the producers and that they are not apathetic towards the consumers' requirements. Variability, however, is a problem which does not appear to have an immediate solution because it seems to be caused, for the most part, by inherent variations in latex; these variations are the result of differences in the trees themselves, in the soil and other environmental conditions under which they are growing, or in the methods used on the estate. Such differences are either outside of human control or are a necessary consequence of economic conditions. The conclusion expressed by Sackett⁹ that the consumer must bear the burden of eliminating most of the variation by blending is unfortunately still a true statement of the position.

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LOW-TEMPERATURE SET AS A MEASURE OF STATE OF VULCANIZATION *

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In his various patents on vulcanization, Charles Goodyear made several references to the change produced in the low-temperature behavior of rubber. In his earliest patent⁷ he stated that vulcanized rubber would not be "injuriously affected by exposure to cold". The reissues of this patent^{8, 9} stated the problem more clearly. "The leading object of my exertions was to render india-rubber capable of resisting the action of heat and cold within the range of atmospheric temperatures. . . . When compounded with sulfur, by the application of a high degree of artificial heat, I obtained good results, and when compounded with sulfur and the carbonate of lead I obtained the best results." . . . The new product "is water-proof, permanently and highly elastic under all conditions of its use".

Whether Goodyear was referring to the freezing of rubber under tension or under no tension we do not know, but it is probable that he had experienced both effects without distinguishing between them. It is interesting to find now that, one hundred years later, rubber chemists are still looking at this change in low-temperature behavior which he recognized as an effect of vulcanization, and are using the effect as a measure of degree of vulcanization.

In recent years the T-50⁶ test has gained considerable popularity as a quantitative measure of the tendency of rubber to freeze under tension. Its popularity is justified, since it can be applied over a broad range of cure and since it measures very precisely a seemingly fundamental property of rubber. It is, however, not the only means of expressing this effect quantitatively. The purpose of the present paper is to demonstrate a simpler method which yields surprisingly precise results, in spite of the fact that none of the usual scientific equipment is used and no measurements other than length measurements are required. Although other papers have approached this subject^{1, 5, 12-15}, none has as yet offered a simple substitute for T-50.

METHODS COMPARED

In the T-50 test a sample of cured rubber is stretched to a predetermined elongation at 20° C., chilled to -70° C., and released. The temperature is then raised at a controlled rate, and the test-piece retracts. The temperature at which it has recovered 50 per cent of the original elongation is called the T-50 temperature.

The equipment required consists essentially of a stretching clamp in a Dewar flask filled with acetone, a cooling bath of acetone and solid carbon dioxide surrounding coils through which the acetone of the Dewar flask is circulated, and a suitable heater for raising the temperature at a controlled rate.

In the 0° set test the sample is stretched to a predetermined elongation, immersed in ice water for 2 minutes, released, held in ice water 1 minute, and

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measured. The result is expressed as "per cent set", based on the original unstretched length, or as "fractional set", based on the initial elongation.

The equipment for the 0° set test consists of a stretching clamp and a constant-temperature bath. The temperature of melting ice (0° C.) is the easiest constant temperature to maintain experimentally, and is used for that reason, although within certain limits any other constant temperature would be suitable. All that is required is a copious supply of ice and a fair degree of forced circulation.

CONDITIONS OF TEST

In the work reported here, three typical compounds have been used: a tread compound, a high-zinc compound and a low-zinc compound.

TABLE I
COMPOUNDS TESTED

	Compound A	Compound B	Compound C
Rubber	100	100	100
Channel black	50	—	—
Zinc oxide	5	120	50
Sulfur	3	2.5	4
Mercaptobenzothiazole	1	0.5	0.5
Stearic acid	4	1	1
Pine tar	5	—	—
Phenyl- β -naphthylamine	1	—	—
	169	224.0	155.5

The effects of the variables of testing will be illustrated by data on compound A. In Table II it is evident that time of freezing between 0.5 and 5 minutes has only a very slight effect. Time of retraction between 0.5 minute and 2 minutes has even less effect. Purely as a matter of standardization, the values of 2 minutes' freezing and 1 minute's retraction have been adopted.

Degree of initial stretch is more important. The data of Table II, if plotted,

TABLE II
CONDITIONS OF TEST*

Original stretch (%)	Time of freezing (min.)	Set after various retraction times			
		0.5 min. (%)	1 min. (%)	0.5 min. (%)	2 min. (%)
300	0.5	136	133	133	133
—	1	136	133	133	133
—	1.5	140	137	137	136
—	2	140	139	138	136
—	3	142	140	139	138
—	5	145	144	142	142
400	2	188	188	186	186
500	2	203	201	198	198
100	2	8	8	8	8
200	2	66	64	64	63

* Work done on sheets of compound A cured 70 minutes at 126.6° C. Test strip was 4 × 2 mm. Each figure is an average of three tests. Procedure: Stretch at room temperature, freeze at 0° C., release, and measure. Set expressed as % of initial length.

indicate that at an original stretch of 100 per cent there is practically no set. At 200 per cent, however, a very definite amount of freezing can take place.

Thereafter, as the initial stretch is increased, the per cent set increases progressively. If this is expressed as a fraction of the initial stretch, it appears that beyond about 300 per cent the fractional set is not increased by further stretch and might even pass through a maximum.

This work was repeated at three cures (Table III, Figures 1 and 2). There are evidently experimental difficulties in picking the maximum (if any), but it ap-

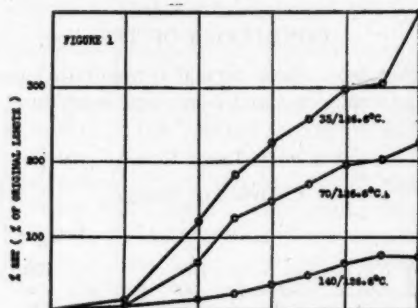


FIG. 1.—Per cent set vs. initial elongation.

TABLE III
EFFECT OF DEGREE OF STRETCH*

Elongation (%)	35-minute cure	70-minute cure	140-minute cure
A. PER CENT SET BASED ON INITIAL UNSTRETCHED LENGTH			
100	15	6	6
200	122	66	16
250	183	125	22
300	226	147	35
350	257	170	48
400	297	195	63
450	305	203	75
500	400	225	73
B. RETAINED FRACTIONAL SET			
100	0.15	0.06	0.06
200	0.61	0.33	0.08
250	0.73	0.50	0.09
300	0.75	0.49	0.12
350	0.74	0.49	0.12
400	0.74	0.49	0.16
450	0.68	0.45	0.17
500	0.80	0.45	0.15

* Each figure is average of four tests. All work done at 0° C. according to procedure of Table II, using 2 minutes' freezing and 1 minute's retraction. All samples are compound A, cured at 126.6° C. as indicated. Retained fractional set is set, as in A, divided by elongation.

pears that at the best cure and the undercure the fractional set increases to an initial stretch of 250 to 300 per cent, while at the overcure it increases to about 400 per cent. At the undercure, moreover, something else happens beyond 450 per cent, which brings about an even higher set. None of the possible explanations for this has been investigated.

As a characteristic measure of state of cure, the fractional set could be considered to be practically independent of elongation between the limits 250 and

400 per cent. However, for everyday use in compounding problems or as a control, it is more convenient merely to standardize on 300 per cent elongation for tread type stocks (550 per cent for most other stocks) and express the result as per cent set, meaning per cent of original length.

The effect of freezing temperature was illustrated by curing a set of sheets of tread stock at ten logarithmically spaced time intervals, and testing at three bath temperatures: 9°, 0° and -9° C.

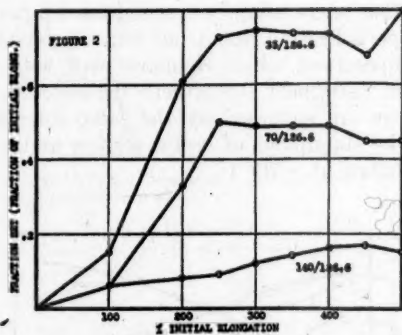


FIG. 2.—Fractional set vs. initial elongation.

TABLE IV

EFFECT OF BATH TEMPERATURE*

Cure at 126.6° C. (min.)	Set at +9° C. (%)	Set at 0° C. (%)	Set at -9° C. (%)	500% modulus (kg./sq. cm.)
30	208	242	253	119
35	192	224	248	148
42	152	214	238	178
50	100	192	225	199
59	55	170	217	212
70	30	136	197	227
85	19	87	172	248
100	17	58	148	250
118	17	39	127	260
140	19	28	99	269

* Each set figure is average of three tests, each modulus average of two. Work done at three bath temperatures as indicated according to procedure of Table II, using 2 minutes' freezing and 1 minute's retraction. Initial elongation 300%. Compound A.

It will be noted (Table IV, Figure 3) that at each temperature the set is high at the undercure and low at the overcure, and that the point in cure at which the most rapid transition from high to low set occurs is a function of the freezing temperature. The lower the freezing temperature the higher the set for a given time of cure, and the higher the state of cure at which the rapid transition from high to low set takes place. It is possible to read from the curves a property which is analogous to T-50. The 9° C. curve crosses the 150 per cent set coördinate (0.5 fractional set) at a cure of 42 minutes. To put this in the language of T-50, we may say that the 42-minute cure has a 0.5 fractional set temperature of 9° C., i. e., it retracts to one-half of its initial stretch at 9° C. Regarding the

other curves in similar fashion and interpolating a combined sulfur curve, we get the following:

Time of cure (min.)	Temperature for 0.5 fractional set (° C.)	Coefficient of vulcanization (%)
42	9	1.04
65	0	1.66
98	-9	2.32

There is a straight-line relationship between these temperature and combined sulfur data, with a slope indicating that 1 per cent combined sulfur is equivalent to 14° C. in bath temperature, which compares well with the published value of 13° C. in T-50. This agreement strengthens the belief that set measurements at constant temperature are governed by the same fundamental properties as T-50, and that from the standpoint of useful results, at least, nothing has been lost by omitting the chilling at -70° C.

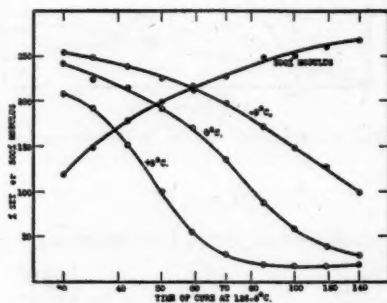


Fig. 3.—Set at various temperatures vs. time of cure.

VARIATIONS IN THE FORMULA

Previously published work has shown definitely that T-50 is more closely connected with combined sulfur than with any physical property^{6, 10, 16}. This is found true also with the 0° set test, although there is evidence that the correlation is not perfect.

The effect of variability of carbon black on the rate of cure of a mercapto-benzothiazole stock is often underestimated, because the changes in modulus and tensile that it produces, particularly in the range of the optimum cure, are rather slight. However, the 0° set test penetrates beyond these physical effects, and reveals the true effects on combined sulfur. In Table V is a comparison of a fast- and a slow-curing channel black having widely different set and combined sulfur values at equal times of cure, but very slight differences in modulus (Figure 4). However, when cured to equal set values, they have nearly equal combined sulfur (Figure 5).

Fast- and slow-curing zinc oxides³ also have a comparatively slight effect on modulus, but the effect on 0° set is so marked that sharp divisions in state of cure are easily made (Table VI, Figure 6). Again the agreement of set with combined sulfur is close, but not exact (Figure 7). The same is true of fast- and slow-curing rubber (Table VII, Figure 8), and it is interesting that the slow-curing rubber

TABLE V
SET AND COMBINED SULFUR AS AFFECTED BY BLACK^a

Cure at 126.6° C. (min.)	Coefficient of vulcanization	0° set (%)	500% modulus
BLACK A			
35	0.86	225	117
50	1.38	186	172
70	1.75	141	201
BLACK B			
35	1.09	206	128
50	1.59	149	182
70	2.05	86	203

^a Compound A with two channel blacks, normal (A) and fast-curing (B). Coefficient of vulcanization is % of combined sulfur based on rubber content.

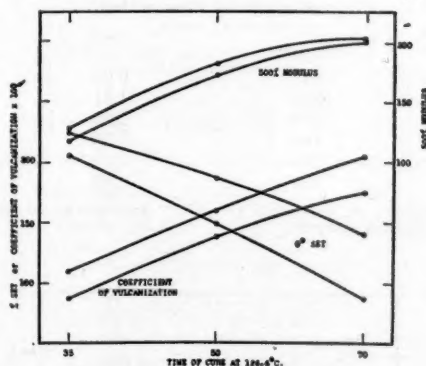


FIG. 4.—Fast- and slow-curing carbon black.

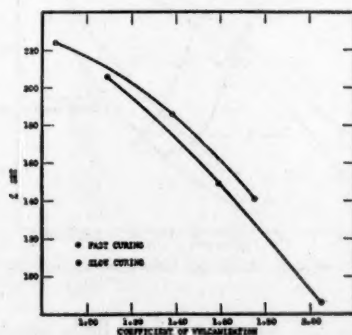


FIG. 5.—Agreement of set and combined sulfur carbon black.

has other effects on modulus, so that when cured such times that it has the same combined sulfur as the fast-curing rubber, its modulus is lower²; for example, at the 140-minute cure the slow rubber has a combined sulfur of 1.38. This com-

TABLE VI
COMPARISON OF ZINC OXIDES^a

Cure at 126.6° C. (min.)	700% modulus	Coefficient of vulcanization	0° C. set (%)
SLOW-CURING ZINC OXIDE			
30	98	—	435
40	129	—	400
50	145	0.84	350
60	160	0.95	240
70	168	1.07	100
80	175	1.18	40
100	182	1.48	—
120	184	1.62	—
FAST-CURING ZINC OXIDE			
30	117	—	420
40	140	—	330
50	152	0.99	210
60	165	1.11	50
70	175	1.24	25
80	184	1.36	—
100	189	1.62	—
120	195	1.83	—

^a Two zinc oxides compared in compound C. 0° C. set determined according to procedure of Table III using initial elongation of 550%.

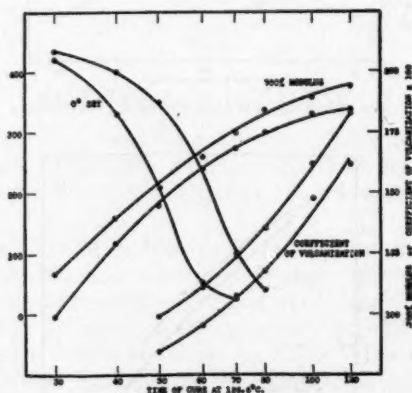


FIG. 6.—Fast and slow zinc oxides.

bined sulfur is reached by the fast rubber in a little less than 100 minutes. The modulus figures are, respectively, 108 and 125. Again combined sulfur and cold set are closely related (Figure 9).

The data of Tables VIII to X and Figures 10 to 12 are included as further evidence that 0° set is unrelated to modulus. Unfortunately, combined sulfur

data are not available. It is possible to vary the total sulfur in a tread stock over the range from 1 to 3 of sulfur and still practically duplicate the modulus. It is known by experience that with high acceleration and low sulfur, we produce a given physical effect with less combined sulfur. Zero degree set (Figure 10)

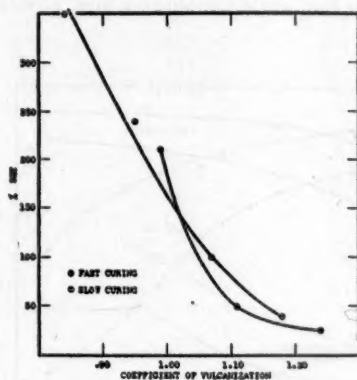


FIG. 7.—Agreement of set and combined sulfur, zinc oxides.

TABLE VII

COMPARISON OF FAST- AND SLOW-CURING RUBBER*

Cure at 126.6° C. (min.)	500% modulus (kg./sq. cm.)	Coefficient of vulcanization	0° C. set
SLOW-CURING PALE CREPE			
50	62	0.71	431
70	80	0.79	419
80	88	—	405
90	92	—	390
100	95	1.07	378
120	101	1.19	365
140	104	1.46	330
200	108	—	250
FAST-CURING PALE CREPE			
50	108	1.02	370
70	118	1.21	338
80	123	—	315
90	124	—	290
100	126	1.48	270
120	128	1.70	195
140	130	1.79	150
200	128	—	60

* Two types of rubber compared in compound B. 0° C. set determined according to procedure of Table III using initial elongation of 550%.

varies in the same order as this prediction of combined sulfur. It is affected greatly by the change in formula, while the physical effect is negligible.

As opposed to this, the amount of fatty acid has a very great effect on the physical properties of a tread stock, but its effect on combined sulfur is small. Figure 11 shows some change in 0° set as acid is varied, but a much greater change in modulus, and in fact a development of modulus in the high-acid stock that

cannot be attained in the low-acid stock. In other words, this represents a large physical effect, accompanied by a relatively smaller effect on set.

The amount of zinc oxide used for activation in a tread stock has a marked effect on physical properties, the higher zinc oxide developing higher modulus. As opposed to this, there is a small difference in 0° set in the opposite sense (Figure 12), that is, high zinc oxide produces a high physical state but set values indicating a low state.

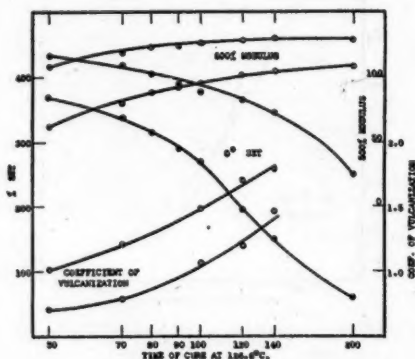


Fig. 8.—Fast and slow rubber.

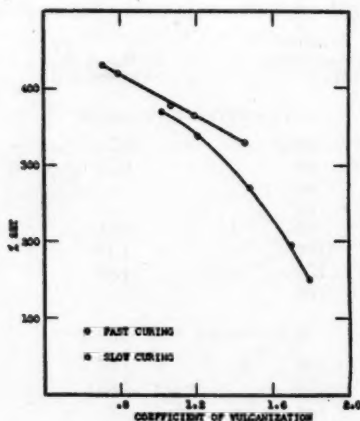


Fig. 9.—Agreement of set and combined sulfur, rubber.

All these compounds, with the exception of the nonsulfur stock (Table VIII), may be considered as normal, present-day compounds. With all the normal stocks, set is high at the undercure and low at the overcure. The transition from high to low is gradual at first, then rapid, and finally gradual again. The point of rapid transition is merely the point in cure at which the 0° set test becomes most sensitive. If a different bath temperature were used, it would be most sensitive at some other cure (Figure 3). Fortuitously enough, with 0° bath temperature the rapid transition takes place near what is considered the optimum cure, and for that reason it becomes a useful tool in development work, provided due consideration is given to the formula variables that are being investigated. To be

TABLE VIII
AMOUNT OF SULFUR*

Parts of sulfur.....	0	1.0	1.5	3.0
Parts of tetramethylthiuram disulfide	3.0	0.25	0.1	—
Parts of mercaptobenzothiazole	—	1.5	1.5	1.0

Cure at
126.6° C.
(min.)

Modulus 500%

35	182	143	148	145
50	195	194	197	198
70	197	223	225	218
100	203	243	243	246
140	215	258	259	255
200	213	—	—	—

0° C. set

35	192	250	225	212
50	187	212	175	125
70	204	150	75	50
100	191	62	43	37
140	188	44	36	40
200	184	—	—	—

* Stocks are compound A with sulfur and accelerator varied as indicated.

TABLE IX
AMOUNT OF FATTY ACID*

Parts of stearic acid

0 2 3 4

Modulus 500%

Cure at
126.6° C.
(min.)

35	80	111	123	134
50	128	170	183	192
70	162	206	222	233
100	183	231	251	262
140	187	243	268	282

0° C. set

35	214	212	211	210
50	196	177	170	161
70	148	101	80	67
100	77	28	25	25
140	28	19	19	19

* Stocks are compound A with stearic acid varied as indicated.

TABLE X
AMOUNT OF ZINC OXIDE*

Parts of zinc oxide

1.0 1.5 2.0 3.0 4.0 5.6

Modulus 500%

Cure at
126.6° C.
(min.)

35	151	140	146	134	133	132
50	177	186	191	196	188	190
70	196	212	227	232	230	223
100	206	229	252	263	263	257
140	194	232	269	280	283	274

0° C. set

35	197	213	214	216	219	220
50	147	168	173	167	180	179
70	59	69	85	83	98	114
100	22	25	27	31	41	40
140	17	19	19	23	25	25

* Stocks are compound A with zinc oxide varied as indicated.

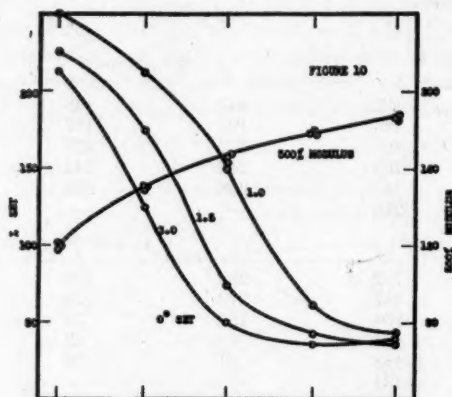


FIG. 10.—Various amounts of sulfur.

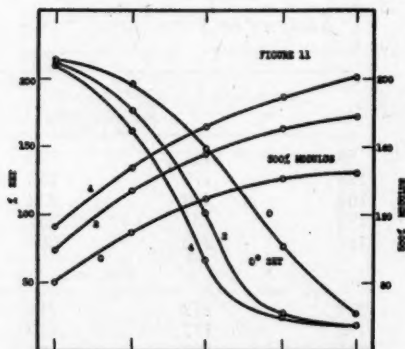


FIG. 11.—Various amounts of stearic acid.

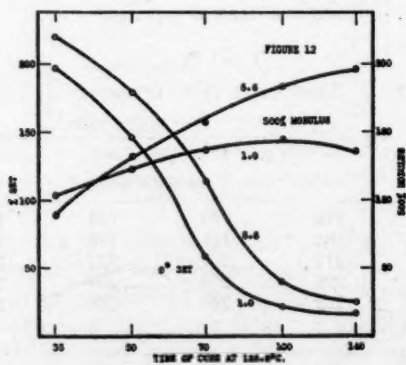


FIG. 12.—Various amounts of zinc oxide.

more specific, an estimation of time of cure to reach this point of rapid transition or to reach any chosen value of set falling within this range immediately gives us the time of cure required to reach a standard state of cure—call it optimum or anything else. The nonsulfur stock does not exhibit this behavior, but it is the writer's opinion that the reason is merely that 0° bath temperature is too low and that at a higher temperature such behavior would be found.

USE AS A CONTROL

In control problems we are interested more in the sensitivity of a test to variations in the raw material than in the numerical significance of the results. Carbon

TABLE XI
COMPARISON OF CARBON BLACKS*

500% modulus, 0° C. set							
Black	Treatment (° C.)	35-min. cure	70-min. cure	70 min. cure	Net volatile	pH	Rebound
SERIES I							
C	None	94	180	159	8.1	—	67.8
D	None	107	190	153	7.3	—	64.4
E	None	111	186	142	5.3	—	59.2
F	None	110	186	133	6.7	—	66.0
G	None	128	204	125	5.6	—	64.8
H	None	122	200	123	5.8	—	68.6
I	None	114	189	120	5.5	—	59.1
SERIES II							
J	None	117	201	141	6.1	—	64.9
K	None	128	203	86	4.9	—	63.2
SERIES III ^b							
L	None	129	200	94	5.3	4.5	63.9
	350	121	201	122	6.2	3.8	—
	500	105	187	153	6.2	3.8	—
	700	135	210	122	5.8	4.2	—
	900	178	225	69	4.1	4.9	—
	1000	175	230	66	3.5	6.4	—

* Channel blacks compared in compound A. Stocks cured at 126.6° C. Net volatile determined by method of Johnson¹¹. pH by method of Wiegand¹². Rebound is average of two tests each at 85 and 140 minutes' cure, determined on pendulum⁴.

^b Treatment consisted in heating with free access to air for 30 minutes at temperature indicated.

black, particularly when the oxygen content of its surface varies, has a considerable effect on rate of cure. One means of estimating this effect is the volatile loss of 950° C. This is a purely arbitrary test, but we know that when the volatile loss is high the oxygen content is high and the rate of cure will be low.

It has been shown above that there is no necessary connection between the numerical values of set and modulus. This is because modulus is affected by so many other things besides combined sulfur. In the case of carbon black it is affected considerably by the reinforcing action of the black in the range of the optimum cure and beyond. As a result, changes due to the retarding effects of different types of black are masked and a certain numerical value of modulus does not indicate any definite state of cure. However, at a distinct undercure the reverse is true, and in compound A the modulus at the 35-minute cure is

sensitive to variation in rate of cure in carbon black. It can be used as a practical indication of rate of cure, even though the compound is to be used at much higher states of cure.

Zero degree set as a control test should be used at the cure at which it is most sensitive and for compound A this is in the neighborhood of 70 minutes. In Table XI is shown a series of channel blacks having varying effects on rate of cure as well as a variation in other properties. Inspection of the table reveals good agreement between these three measures of rate of cure. Zero degree set at 70 minutes and modulus at 35 minutes are well in line, low set and high modulus going together in indicating a high rate of cure. There is likewise a parallelism between set and net volatile, low set and low volatile going together. As a matter of interest, correlation coefficients (Pearson's) for these two comparisons are: for set of modulus -0.90 ± 0.03 and for set and volatile 0.87 ± 0.04 . Both figures indicate a high degree of correlation.

DISCUSSION

It must be admitted that the 0° set test will not cover the almost unlimited range of cure that the T-50 test will. However, it is applicable over a good part of the curing range of most present-day tire compounds and for that reason it is not at a practical disadvantage. It has the definite advantage of simplicity in equipment, cooling medium and manipulation, and as a control test could be operated by a person unaccustomed to chemical laboratory equipment. In gaining this simplicity no precision has been lost.

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VULCANIZING FROM A THERMODYNAMIC VIEWPOINT *

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The application of thermodynamics to the study of organic processes has only recently been undertaken extensively and has been confined largely to simple substances which can be readily analyzed and purified. The study of reactions involving more complicated substances, such as resins and gums, has seldom been attempted because the more simple methods of attack, such as reaction equilibrium, are not possible. The study of such systems is further complicated by the indefinite nature of the substances and the difficulty of closely identifying either starting materials or end products. The application of thermodynamics to the study of vulcanization has only just begun, and the present discussion must be limited to correlating the small amount of available data and to indicating desirable fields for future investigation.

The most valuable tool of thermodynamics, when applied to chemical reactions, is the free energy ΔF , which is a measure of the driving potential of the reaction; it indicates the ability of the reaction to proceed spontaneously. The relation:

$$\Delta F = RT \ln K$$

where R = gas constant

T = absolute temperature,

permits the equilibrium constant K of the reaction to be determined, and the way is open for predicting the effect of other variables. Such calculations are not ordinarily concerned with the intermediate processes of the reaction, but require definite information in regard to both the starting materials and the final or equilibrium products.

It is then necessary, before applying thermodynamics to the study of vulcanization, to define vulcanization clearly in terms of the final product. At present this is not entirely possible. Certain factors are recognized, for example, the combination of sulfur. However, the amount of combined sulfur cannot be used to define vulcanized rubber because under some conditions sulfur will combine without producing vulcanization²⁰. Furthermore, it is known that the same amount of combined sulfur does not always produce the same type of vulcanized rubber^{16, 27}. Vulcanization involving chemical reactions other than combination of sulfur is known. Rubber becomes useful after vulcanization because it has acquired new physical properties. This change is common to all types of vulcanization in varying degrees. It must also be recognized that rubber has a rather narrow temperature range of usefulness, and that the physical properties must be determined within this temperature range. With these factors in mind, we may conclude that vulcanization is a decrease in the plasticity of rubber within its elastic temperature range. Although a physical definition of vulcanization may be important for determining the extent of change, the chem-

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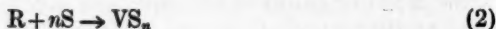
ical reactions cannot be disregarded, since the energy changes involved in the chemical processes may entirely overshadow those directly responsible for the vulcanized properties.

VULCANIZATION REACTIONS

Several reactions may be proposed for explaining the process of vulcanization, and a few of the possible ones will be used as a basis for further discussion. In the following equations R represents raw rubber, V represents vulcanized rubber, S represents sulfur or any other element or radical which adds to the rubber, and A represents an accelerator of vulcanization.



This equation assumes that the mechanism directly responsible for vulcanization does not involve the combination of an added material with the rubber.



This equation assumes that vulcanized rubber is a chemical derivative of rubber.



This equation assumes that part of the rubber reacts chemically to produce a derivative of rubber, while the remainder becomes vulcanized. The vulcanization and chemical attack may be in different molecules or, in the case of extremely large molecules, chemical attack insufficient to destroy the elastic properties would induce the remainder of the molecule to become vulcanized.



This equation assumes that accelerator, a metal and a chemical reagent all combine with rubber to cause vulcanization. This equation might well be supplemented by showing a separation of the final product VSAZn into VS + AZn.

These equations by no means represent all of the possibilities suggested, but serve to present the problem in an increasingly complicated aspect and will be presented in this order.

REACTION 1

Both raw and vulcanized rubber may be considered as steps in the evolution of certain chemical substances from a high to a low energy level. Although the actual mechanism of the synthesis of rubber by plants is not known, the process is probably photosynthetic and capable of establishing the parent substance of rubber at a high energy level. Regardless of the parent substances, raw rubber is formed as an unsaturated hydrocarbon. Measurements of the free energies of formation show that unsaturated hydrocarbons are thermodynamically unstable with respect to the elements of which they are composed and with respect to other hydrocarbons²⁸, and under suitable conditions are capable of transformation into more stable substances. The measurements of Bekkedahl and Matheson^{1,2} show that the free energy of formation, $\Delta F^\circ_{298.2}$, of rubber has a value of $22,500 \pm 1600$ calories per mole of C_6H_8 , the positive value indicating instability with respect to its elements. This compares with a value of 50,840 for acetylene and 12,300 for ethylene, both of which are unstable and can be readily transformed to substances having lower energy levels.

Such an indication of thermodynamic instability does not require rapid decomposition or reaction. It indicates rather the possibility of a change which may be extremely slow unless favorable conditions, such as changes of temperature or pressure or the application of a catalyst, are imposed. Such a metastable condition exists in raw rubber, which will remain unchanged for years under ordinary conditions.

Although Equation 1 does not include the polymerization of such dienes as 1,3-butadiene, isoprene and chloroprene, it is necessary to consider them because of the rubberlike polymers which they readily form. This is especially necessary because, under suitable conditions, certain conjugated dienes can be polymerized into forms which resemble either unvulcanized or vulcanized rubber, and may in the future provide information regarding the relation between the plastic and elastic state.

The free energies of isoprene and purified rubber were determined by Bekkedahl¹. Their measurements were made by an application of the third law through the relation:

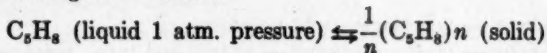
$$\Delta F = \Delta H - T\Delta S$$

where ΔH = heat of formation

T = absolute temperature, ° K.

ΔS = increase in entropy of the system

The values for the heat of formation of rubber were determined directly by Jessup and Cummings²⁰ and the value for isoprene by Jessup¹⁹. Bekkedahl and Matheson² and Bekkedahl and Wood³ determined the heat capacities of rubber and isoprene over a temperature range extending sufficiently low to permit a determination of ΔS . The free energies of formation, $\Delta F^\circ_{298.2}$, were calculated to be $22,500 \pm 1600$ calories per mole for rubber and $33,110 \pm 680$ for isoprene; the mole in each case is considered to be the unit C_5H_8 . The value for the free energy change during the reaction:



was then calculated to be $-10,700 \pm 1600$ calories per mole. This shows that at 25° C. the change can be spontaneous in the direction of rubber, since rubber exists at a lower energy level and is more stable than isoprene.

The admirable work of Bekkedahl and his associates has provided a basis for the application of thermodynamics to the study of rubber. The measurements made with isoprene and natural rubber show that it is possible for isoprene to polymerize spontaneously into rubber. Determination of the dissociation constant shows that the reaction can proceed toward rubber almost completely at any temperature below about 600° K.

Unfortunately for the production of rubber, the data of Bekkedahl and his associates do not require isoprene to polymerize into rubber, and experience has revealed that side reactions produce a variety of other products, sometimes almost to the exclusion of rubberlike polymers. This makes it desirable to determine ΔF for the more important side reactions, in order that the dissociation constant may be calculated and conditions determined for avoiding such products as terpenelike dimers and high-molecular-weight inelastic polymers. The free energy of the rubberlike polymer (which does not have the properties of unvulcanized natural rubber) should also be determined.

Polymerization of isoprene can produce a polymer with vulcanized properties. This is especially true if the polymerization is conducted under pressures of

10,000 to 18,000 atmospheres and at ordinary temperature as was done by Conant and Tongberg¹². The products of this polymerization were not only almost completely insoluble but were also nonplastic³⁶. The polymerization of isoprene under these conditions gives a product which closely resembles vulcanized rubber and may be found to be at an energy level somewhat below that of unvulcanized rubber.

The formation of a vulcanized type from a liquid diene is illustrated more clearly in the case of chloroprene (2-chloro-1,3-butadiene). This material polymerizes rapidly and spontaneously to form a rubberlike product¹¹. If polymerization is interrupted in the early stages and the polymer recovered, it is found to resemble unvulcanized rubber closely in being elastic, soluble and plastic. This plastic material will proceed to change spontaneously in the course of a few days into an insoluble, nonplastic vulcanized type.

The change from chloroprene directly into the vulcanized type of polymer takes place with considerable evolution of heat. If chloroprene is emulsified in a dilute sodium oleate solution, polymerization is sufficiently rapid, so that the heat of the reaction can be easily determined. Measurements conducted by Walker³³ show an evolution of 15,130 calories per mole at 30° C. with a possible error of ± 5 per cent. This is somewhat less than the change from isoprene to unvulcanized rubber, although chloroprene polymerizes much the more readily. No measurements are available for the change chloroprene \rightarrow plastic polymer, and so the energy relation between the plastic and elastic polymers is not known. Since chloroprene diluted with an inert solvent such as carbon tetrachloride does not readily polymerize beyond the plastic stage, it should be possible to determine the heat of polymerization to the plastic polymer which corresponds to the unvulcanized state.

Such a study of the polymerization of chloroprene or isoprene may, however, be quite misleading, because it is necessary to assume the identity of the initial and final states in the two reactions:

Diene \rightarrow vulcanized-type polymer

Diene \rightarrow plastic polymer \rightarrow vulcanized-type polymer

In each case the vulcanized polymer is elastic and nonplastic. Observations, however, indicate that although both are a vulcanized type, they differ in physical properties. The direct polymer produced from either isoprene or chloroprene appears from hand examination to be deficient in elastic properties, since it is relatively hard and breaks with a glassy fracture at a low elongation. The change from plastic to elastic chloroprene polymer produces a vulcanized type which is softer and has a much higher tensile strength and elongation at break than the product resulting from direct polymerization to the vulcanized type. The difference appears to be more than could be accounted for by the degree of vulcanization of the plastic polymer. In the case of isoprene, the products of the two processes cannot be compared, since as far as is known a truly plastic polymer of isoprene uncontaminated with large volumes of unpolymerized isoprene, added ingredients, or the products of side reactions, has never been obtained.

Considerable doubt exists that unvulcanized rubber represents a plastic isoprene polymer. Conant and Tongberg¹² showed that polymerization inhibitors are often of little effect at high pressures, but in spite of this favorable circumstance the application of high pressure to raw rubber containing dissolved isoprene does not produce a vulcanized rubber⁴⁰.

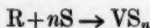
However, rubber is capable of rapid spontaneous changes into new products under the proper conditions. This is illustrated by the various isomers of rubber which are produced under the influence of catalysts^{10, 13}. These isomers are produced with a decrease in unsaturation and a large evolution of heat. Rubber also changes when heated alone to a temperature of 270° C.³⁰ to form a product which is more stable than rubber, and which will no longer yield isoprene on destructive distillation. Although such a change is not vulcanization, it shows the possibility of a spontaneous change from rubber to a product with new properties.

Raw rubber can be made to assume a somewhat vulcanized form by the incorporation of a sufficient volume of finely divided pigments. Menadue²⁴ studied such pigments as carbon black, zinc oxide, magnesium carbonate and clay, and found that an increasing amount of insoluble rubber was produced as the volume of pigment was increased. The addition of a sufficient volume of carbon black produces an insoluble and nonplastic compound. This effect need not be confined to the molecular layer of rubber on the carbon interface, since the effect of a surface-generated force can extend many molecular layers from the surface. This is well illustrated by the study of the effect of interfacial distances on the polymerization of chloroprene⁴¹. Spear²⁸ and Blake⁴ developed the concept of free and bound rubber to explain the reinforcing effect of pigments, and the idea can be extended to explain insolubility and loss of plasticity. Menadue, however, points out that removal of the pigment, which in the case of materials such as zinc oxide or magnesium carbonate can be done with acid, does not restore the rubber to a soluble condition but leaves it permanently altered. Wiegand³⁵ also suggests an alteration in the type of rubber at the rubber pigment interface.

Attempts have been made to determine the heat effects associated with the incorporation of pigments into rubber. Boström⁸, Hock¹³, Hartner¹⁷ and Blake⁷ measured the heat of wetting of carbon black by rubber. This work is discussed by Wiegand³⁵ who points out the difficulty in determining the source of the heat which was measured. The actual amount of heat evolved, according to Hartner, is only about 3.6 calories per gram of black. If the rubber composition was one third carbon, the heat liberated would be only 122 calories per mole (C₅H₈) of rubber. This is even less than the error of measurement of ΔH for the reaction $C_5H_8 \rightarrow (1/n) (C_5H_8)_n$. In view of these figures the insolubility caused by pigments is probably due to physical rather than to chemical changes.

REACTION 2

The thermochemistry of this reaction:



seems to offer no particular difficulty. There is difficulty, however, in determining the identity of the end product. This difficulty is immediately apparent when the relation between state of vulcanization and amount of combined sulfur is examined. Shepard and Krall²⁷ and Hardman and White¹⁶ showed that no relation exists between the amount of sulfur which combines and the resulting physical properties. The end product cannot then be the simple product VS_n, but must at least consist of two products which hold the sulfur in a different type of combination or combined in a different position in the rubber molecule. Such methods of combination have been proposed⁵. It appears to be possible, however, to isolate a continuous series of fractions from vulcanized rubber, which are each mixtures and not pure substances and which contain varying amounts of

sulfur³⁸. Under such conditions, definite interpretation of simple thermochemical measurements of the combination of sulfur is not possible.

If two entirely different types are present, as proposed by Blake, the H values for each reaction should also be different. If only one of these reactions is responsible for vulcanization, it should be possible to choose two rubber compounds—one which changes physical properties rapidly with low combined sulfur, and the other which combines much sulfur with little change in physical properties—and find a different value for the heat of combination of sulfur in each case.

Combination of rubber with sulfur is accompanied by changes in physical properties not directly associated with vulcanization. Highly purified rubber combined with sulfur with little vulcanization effect, but the continued reaction produces a normal ebonite. Pure isoprene or 2,3-dimethyl-1,3-butadiene polymers combine with sulfur without producing a useful soft vulcanized rubber, but these also produce a product resembling ebonite. McPherson and Bekkedahl³⁸ showed that combination of sulfur produces evolution of heat at a uniform rate until half an atom of sulfur has combined. This is sufficient sulfur to destroy the elastic properties of the rubber and produce an easily recognizable beginning of ebonite formation. This indicates that the heat liberated is directly connected with the formation of ebonite rather than with vulcanization to soft vulcanized rubber.

REACTION 3

Interpretation of thermochemical measurements applied to this equation:



are also difficult, because the end products cannot be defined. If R reacts as a single molecule, it is evident that V must be a smaller unit, and can be formed only by a rupture of a carbon bond. This process would absorb heat and tend to mask or even exceed the heat produced by the combination of sulfur. Since the reactions, as indicated, would be in equivalent amount, the change should show a direct relation between combined sulfur and ΔH . The rubber xR might also be interpreted as being a group of molecules, part of which combine with sulfur and part of which enter into a new physical or chemical arrangement to form vulcanized rubber. A new chemical arrangement might be detectable and produce a different relation between combined sulfur and heat liberated in different compounds. A new physical arrangement would probably involve an energy change beyond the present limits of thermochemical accuracy.

Qualitative and quantitative measures of the heat developed during the combination of sulfur have been made by a number of investigators^{5, 6, 9, 14, 15, 20-23, 26, 32, 34, 39}. An analysis of the various determinations shows that, during the period of vulcanization to form soft rubber, the amount of heat evolved is proportional to the amount of sulfur which combines. Such a picture adds little to our knowledge of the process according to the physical definition of vulcanization.

Blake originally believed that the first few per cent of sulfur combines isothermally with the rubber to produce soft vulcanized rubber. Such a process would probably mean that the reaction with the least chemical potential would proceed first. Since most chemical processes are more or less dominated by catalytic influences, it is possible that the reaction with the least free energy change could proceed to completion before another reaction would assume important proportions. However, the heats of formation of organic sulfur compounds show that reactions of sulfur usually involve a considerable heat effect. If the first

part of the vulcanization reaction is isothermal, it is more reasonable to assume the presence of an endothermal reaction which essentially balances the exothermal reaction of sulfur with rubber. The latest work of Blake⁶, in common with the work of most other investigators, shows that heat is evolved during the entire course of the reaction.

The thermodynamics of sulfur compounds have been little investigated. Data presented by Parks and Huffman²⁵ show that the corresponding oxygen compound is usually much the most stable. Rubber in the presence of both oxygen and sulfur should finally form the oxygen compound rather than the sulfur compound. These reactions, however, are sufficiently slow so that they are readily controlled by means of catalysts.

REACTION 4

No evidence exists that the formation of a compound composed of rubber, sulfur, accelerator and zinc is responsible for vulcanization, although sulfur may be combined with the rubber, the combination of sulfur in the absence of other materials will not produce a useful vulcanization²⁶. Sulfur and either natural or artificial accelerators when heated in pure rubber hydrocarbon will induce vulcanization. The addition of zinc, either as a rubber soluble salt or in the form of a coordination compound with an amine, to the rubber-sulfur-accelerator combination is necessary to produce the greatest change in the rubber. All the materials are necessary to produce the greatest effect, and it is possible that the substance VSAZn is an intermediate in the process of vulcanization and is formed as a coordinate compound after the sulfur has combined with the rubber. So far as is known, the amount of heat liberated by the combination of sulfur in the presence of accelerator is no greater than in its absence, but the rate of the reaction is increased.

It is evident that the heat developed by the combination of sulfur and rubber, when various rubber compounds are compared, is not a measure of vulcanization and may be a composite of the heat for several reactions¹⁴. Sulfur combines with the acetone-extractable substances of rubber, with evolution of heat¹⁹. Jessup and Cummings²⁰ suggested that impurities in the rubber alter the heat of combustion. In the case that both the zinc oxide, fatty acids and accelerators are present, the situation is still further complicated. It might be possible to arrive more nearly at the determination of energy changes associated with the loss of plasticity of rubber if the combustion were determined on a physically well vulcanized, highly accelerated, low-sulfur compound vulcanized in the presence of zinc and thoroughly extracted after vulcanization. Such data should show that the energy changes which accompany the loss of plasticity of rubber and which are induced by the presence of accelerator and zinc^{21, 27}, either are measurable or are of a magnitude usually associated with physical changes.

CONCLUSION

Up to the present time thermochemical data in regard to vulcanization have been concerned largely with the heat of reaction of sulfur. This was a logical first step. The heat liberated is proportional to the sulfur which is combined, and the heat associated with the change in physical properties of the rubber is indicated to be quite small.

A study of the free energy change for the reaction isoprene \rightarrow natural rubber indicates that such a process is possible if the proper conditions can be found. A

study of the thermodynamics of the most important side reactions might help establish conditions for the formation of the rubberlike polymer.

A study of the free energy of the rubberlike isoprene polymer should assist in the comparison of this product with natural rubber.

The vulcanized properties caused by incorporating a finely divided powder into rubber are associated with a relatively small energy change.

A study of the reactions: chloroprene \rightarrow vulcanized polymer and chloroprene \rightarrow plastic polymer \rightarrow vulcanized polymer, appears to be a probable source of information regarding the nature of change from plastic to nonplastic condition.

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STRUCTURAL STUDIES OF THE VULCANIZATION OF RUBBER UNDER STRETCH *

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Just one hundred years have passed since the changes were discovered which rubber undergoes when mixed with sulfur and heated. Although "vulcanization", as this reaction and the changes subsequent thereto have been termed, must be considered the most important development in the rubber industry, we are still far from being in a position to offer a fully satisfactory explanation for this phenomenon. Nevertheless we have been able to improve our concept of these changes by the application of such modern methods of research as x-ray diffraction, and recent attempts to shed more light on the phenomenon from a strictly chemical point of view also have been successful.

The outstanding results of the latter work¹ are the definite proof that the changes in physical properties, which become noticeable during vulcanization, show no correlation with the amount of combined sulfur or with the total loss in unsaturation.

The experiments offered no direct experimental evidence as to the existence of specific chemical bonds or linkages in vulcanized rubber. However, it could be definitely ascertained that chemical reactions involving the double bonds of the hydrocarbon and its combination with the vulcanizing agent, in one way or another, are necessary to produce a vulcanized structure responsible for the observed changes in properties.

On the basis of available data it appears that intermolecular sulfur linkages as a result of dehydrogenation of the rubber-molecule might be considered, at least in accelerated stocks, the most effective type of sulfur-combination in building up a vulcanized structure^{1, 2}. The other alternative, namely, a straightforward polymerization reaction between the double bonds of neighboring rubber molecules, does not seem to explain the optimum tensile strength of the compounds studied.

In the case of soft vulcanized rubber, it is today generally assumed that the sulfur bridging of adjacent hydrocarbon molecules through cleavage of the double bonds takes place in such a manner that the molecules are still free to extend and become parallel with increasing tension.

On the basis of x-ray studies of rubber in unstretched and stretched condition, the assumption is today generally accepted that the long chain rubber molecules line up into a more or less parallel orientation during stretch and thus give rise to a so-called fiber pattern; whereas in unstretched condition random orientation must prevail. If vulcanization is primarily due to sulfur bridging of adjacent hydrocarbon molecules, then vulcanization of rubber under stretch should reveal results which should materially add to our present structural ideas of vulcanized rubber.

The literature on this subject seems to be limited to two U. S. patents.³ Busse obtained a very tough, fibrous rubber, extremely resistant to extension and rupture by stretching rubber short of its normal breaking point and then subjecting

* Reprinted from the *India Rubber World*, Vol. 101, No. 2, pages 31-33, November 1, 1939.

it to the action of an appropriate vulcanizing agent, such as sulfur chloride vapor. Although the patent mentions vulcanizing temperatures from 0-85° C., low temperatures are preferred because the plastic flow of the rubber is then less and the true elongation attainable is greater. Masticated rubber can only be used if given a preliminary vulcanization to overcome the plasticity inherent to unvulcanized milled rubber. According to the patent, rubber treated thus (the best results are obtained with dried latex-rubber sheets) exhibits a pronounced x-ray fiber diagram.

Schade's patent differs from the one above by vulcanizing rubber under such physical stress that the resulting product still retains elasticity. Such rubber will show an ultimate elongation reduced by an amount roughly proportional to the elongation applied during vulcanization. The rubber exhibits a much higher modulus than the same compound, if vulcanized under normal conditions. This patent, too, uses desiccated latex-rubber sheets as most satisfactory. It also refers to the necessity of prevulcanization, if milled rubber is to be used. The maximum stretch during cure, as referred to in this patent, is 400 per cent. Vulcanization according to Schade's process was carried out at temperatures between 135-146° C. in open steam. The patent contains no reference to results of x-ray diffraction, and neither of the two patents gives any indication as to the amount of combined sulfur or related chemical data.

For the purpose of obtaining such information, the following two compounds were prepared:

COMPOUND A

Ingredient	Parts by weight	Function
Latex (60%)	167.00	Rubber
Zinc oxide	2.00	Activator
Sulfur	1.00	Curing ingredient
Butyl zimate	1.00	Accelerator
Darvan No. 1.....	0.16	Dispersing agent
Casein	1.00	Stabilizer
Caustic soda	0.15	Casein solvent
β -Naphthol	0.01	Preservative
Water	8.01	Medium

COMPOUND B

Latex (60%)	167.00	Rubber
Zinc oxide	2.00	Activator
Sulfur	5.00	Curing ingredient
Butyl zimate	1.00	Accelerator
Darvan No. 1.....	0.32	Dispersing agent
Casein	0.24	Stabilizer
Caustic soda	0.10	Casein solvent
Water	7.34	Medium

The compounding ingredients in paste form, as well as the latex, were mixed thoroughly by prolonged rolling of the container in a room refrigerated to 10° C. The compounds were then poured onto a glass plate on which glass strips had been cemented to form a frame. The films were dried at normal room conditions until they could be removed, and hung into a vacuum desiccator in the refrigerated room. After five days, standard test-pieces were stamped out, marked and then kept in the desiccator until ready for cure. Since previous work on the vulcanization of latex compounds had demonstrated that the rate of vulcanization of liquid latex compounds at temperatures below 10° C. is practically negligible and that

vulcanization proceeds extremely slowly when drying vulcanizable latex compounds at room temperature, the procedure as outlined seemed satisfactory for the purpose.

The test-specimens were fixed between clamps of an appropriate stretching machine, were rapidly stretched to the desired elongation, and the whole apparatus was immediately submerged into boiling water. At the termination of the desired time of cure, the apparatus was removed and plunged into ice water. Then the samples were removed, wiped dry, and returned to the vacuum desiccator, held at 10° C.

Before testing the samples for permanent set, tensile strength and modulus on a standard Scott tensile tester, they were brought to room temperature.

Combined sulfur determinations were carried out by subjecting the samples for sixteen hours to extraction with cold acetone, followed by eight hours' hot extraction⁴. The total sulfur was determined on the remaining rubber⁵.

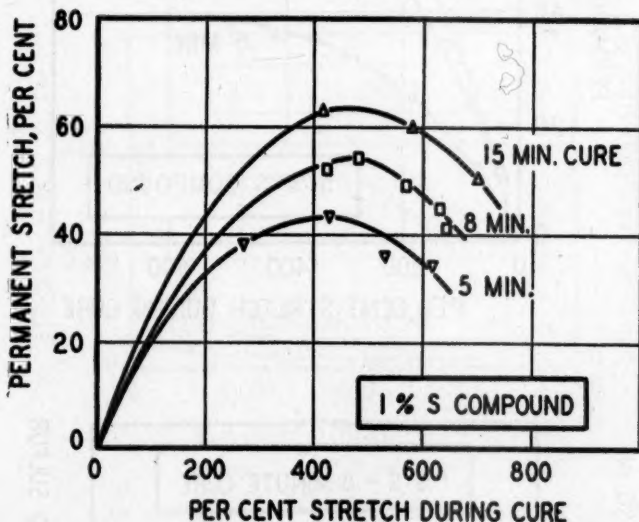


FIG. 1.

The results obtained with Compound A for permanent set *versus* elongation during cure and for different times of cure are plotted in Figure 1. The results obtained with Compound B are represented in Figure 2. Figure 3 demonstrates the changes in tensile strength and modulus and combined sulfur with varying elongations during cure for Compound A; whereas Figure 4 shows the data obtained with Compound B.

The following facts become immediately noticeable. (1) The permanent set exhibits a maximum if the elongation during cure is about 500 per cent. This seems to be independent of time of cure with compounds containing small proportions of sulfur. Compounds containing high proportions of sulfur (for an accelerated soft rubber compound) exhibit the same maximum only for the time resulting in optimum cure. (2) The tensile strength drops with increasing elongation during cure. The modulus at the point of maximum permanent set is either at a minimum or becomes constant from this point on⁶. (3) The combined sulfur for a given time of cure is independent of elongation during cure.

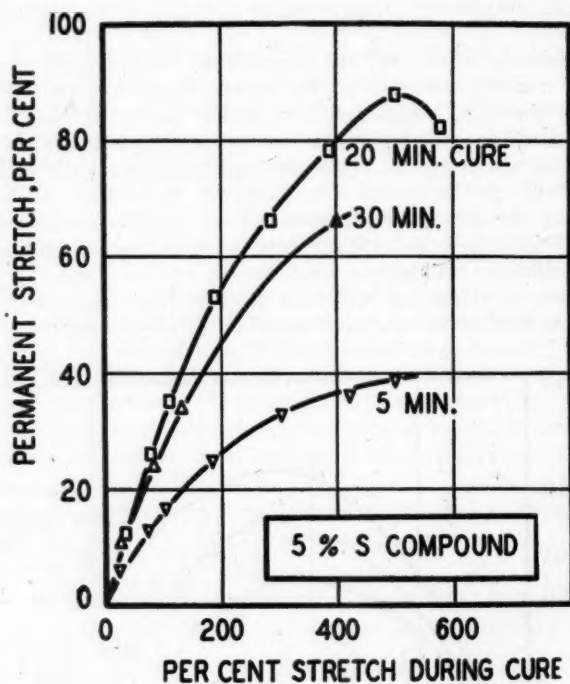


FIG. 2.

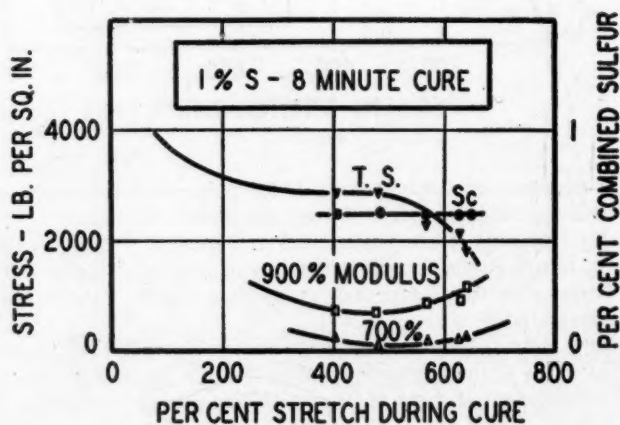


FIG. 3.

All vulcanized samples were submitted to x-ray diffraction analysis. However, no signs of a fiber pattern could be detected, even with those samples which were cured, either under conditions resulting in maximum permanent set, or at a maximum elongation during curing.

Since the recorded permanent sets after cure seemed unexpectedly low, analysis for combined sulfur of the dried but unvulcanized test slabs were made, which revealed a combination of sulfur of 0.14 per cent. To decide if this combination affects the results, test-slabs of Compound A were made, but this time the films were not only poured but also dried in a refrigerated room at about 10° C. Curing and testing were carried out as discussed before. The results obtained are plotted in Figure 5. In this case we find that the permanent set seemingly also tends toward a maximum, but the attainable elongation was insufficient actually to demonstrate such a maximum. The tensiles first drop rapidly, approaching constant values at higher elongation during cure, and the same can be said for the modulus.

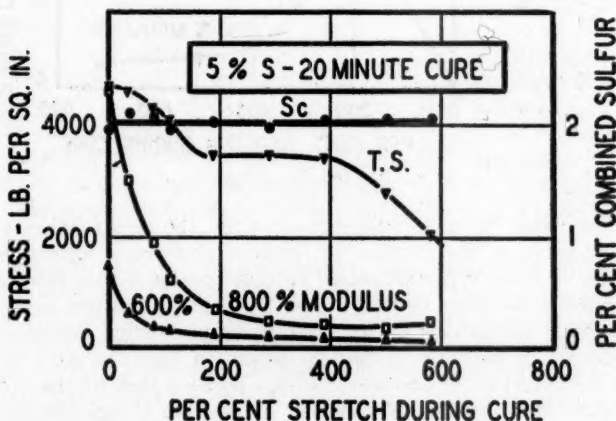


FIG. 4.

In this series, also, no indication of a fiber diagram could be obtained by x-ray diffraction. However, if those samples, which were cured at medium elongations and had retained a certain amount of elasticity were x-rayed while kept under tension, they showed very sharp fiber patterns.

DISCUSSION OF RESULTS

The fact that none of the vulcanized samples revealed even the faintest traces of an x-ray fiber diagram proves beyond doubt that no preferential orientation of the molecules can exist. Since it is known that unvulcanized rubber, if stretched to only a few hundred per cent, shows a preferred orientation of its molecules and since stretched rubber, if vulcanized in sulfur chloride vapors, according to Busse, also exhibits an x-ray fiber diagram, we must assume that a rearrangement of the parallel oriented molecules into random orientation takes place during vulcanization at temperatures above 100° C.

The fact that rubber cured at maximum elongations shows a high permanent set without revealing preferred molecular orientation can be explained by assuming that the molecules, due to their appreciable thermal oscillation at vulcanizing

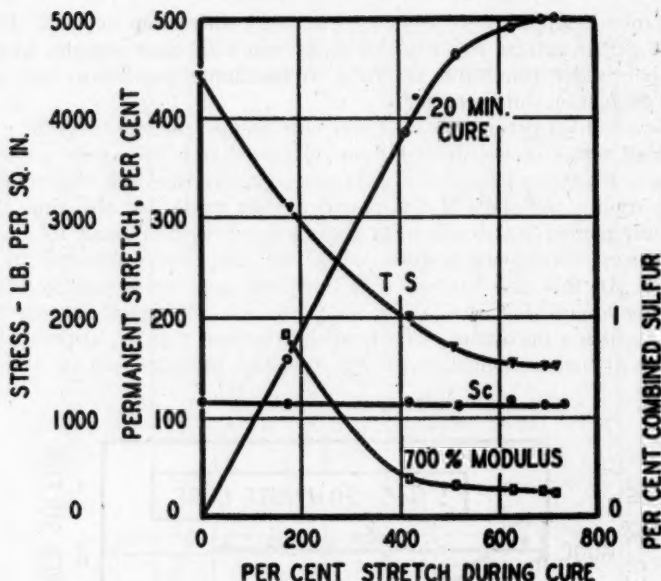


FIG. 5.

temperature, are fixed in an entangled position by the sulfur linkages, thus retaining the elongation of the sample, but without preferential orientation.

If the rubber is already prevulcanized to some degree before final cure in an elongated condition, we must naturally take the existing linkages into consideration. At maximum elongations during cure, these preexisting linkages add their retracting tendency to the effect of thermal oscillation, thus causing a fixing of the molecules by the added sulfur linkages in such a position that contraction becomes clearly noticeable on release of the tension. At medium elongations during cure, the added sulfur linkages balance the influence of the preexisting linkages or even become predominant, because at this stage molecular elongation has not yet reached the point where the tendency to contract is as pronounced as in the previous case.

The more or less constantly decreasing tensile strength with increasing elongation during cure is to be expected, since the more extended are the molecules, the more easily do they transfer the applied force to the weak spots of the system.

No explanation can be offered for the discrepancy of tensile strength data reported above and those reported by Schade.

The results substantiate the contention that the changes which rubber undergoes during vulcanization are primarily due to intermolecular sulfur linkages.

Our thanks are due to the R. T. Vanderbilt Co. for supplying us with the vulcanizing dispersions used in this investigation.

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CONTROL BY INDIVIDUAL INCORPORATION OF VULCANIZING AGENTS *

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The individual incorporation of vulcanizing agents without a concurrent milling operation, *i.e.*, by some form of diffusion process, originated with Thomas Hancock. Sulfur had been previously used as a dusting powder, *e.g.*, by Lüdersdorff in 1832, and the storage of the dusted rubber must have led to gradual penetration of the sulfur into the rubber and possibly to effects of accidental vulcanization, especially if such rubber became exposed to sunlight, as was definitely the case in 1837 in Hayward's solarization process. But Hancock's well-known patent specification¹⁰ gives the first description of the deliberate incorporation of sulfur by a diffusion process for the purpose of subsequent heat vulcanization. This patent also describes and claims the compounding of rubber with mineral fillers and with asphaltum; it explains how "by immersing the caoutchouc in melted sulphur (at a temperature ranging from about 240° to 250° Fahrenheit)" or by "heating sheets of caoutchouc to about 200° and sifting and rubbing flour of sulphur on it" one can blend sulfur with the rubber, so that by subsequently raising the temperature "to 300°, or from 300° to 370° . . . the change is produced". The "change" was the term used by Hancock "for brevity's sake" to describe the desired effect.

In 1857 Hancock gave further details¹¹ of the possibilities of this method of procedure and adds: "This mode of producing the 'change', so unique in many respects, is particularly so in this, that articles manufactured of pure rubber with which no sulphur has been blended may be changed in the sulphur bath; take, for instance, a native South American shoe, immerse it hot in the bath, at the lowest temperature at which sulphur will melt, say 240°, and let it remain until it has absorbed enough sulphur; then gradually raise the temperature to 265° or 270°, and in the course of an hour or something more, according to the thickness, the shoe will be perfectly 'changed.'"

It is noteworthy that this early process of vulcanization in a bath of molten sulfur is still in operation, for the manufacture of thin rubber articles such as tobacco pouches, in the historic factory in which Thomas Hancock and Charles Macintosh were partners in England, and also elsewhere in Europe¹².

The use of a diffusion process for the introduction of an accelerator of vulcanization into an otherwise fully compounded rubber article was also described at a relatively early date. In 1811 Rowley¹⁷ patented several methods for obtaining an improved vulcanized product; one form of his procedure was to vulcanize in the presence of a solution of ammonia or of solutions yielding ammonia. The same principle is further elaborated in a French patent of 1903¹⁸; this process involves hot vulcanization in ammonia gas under pressure.

In a generous interpretation, the compounding of rubber by way of latex provides an example of the control of vulcanization by the individual incorporation of vulcanizing agents. When aqueous dispersions of vulcanizing ingredients such as sulfur and accelerators are added to latex, the particles substantially retain

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their individuality outside the rubber globules; and even when the latex is evaporated to form a film of compounded rubber, their identity is largely maintained. This fact is evident from the slowness with which a sample of compounded latex rubber, after being dried without marked elevation of temperature, yields its free sulfur to acetone extraction, compared with a piece of compounded rubber of similar composition prepared by milling; in the latter case the sulfur is already present, to a considerable extent at least, in solution in the rubber. One of the first effects of the heat applied for vulcanization of such a "latex compound" is to bring the sulfur (and other vulcanizing ingredients) into solution in the rubber phase so that vulcanization can take place.

The present considerations, however, are concerned primarily with the individual incorporation of vulcanizing ingredients into dry or, at least, coherent rubber.

With the advent of ultra-accelerators, the diffusion principle for the incorporation of vulcanizing ingredients subsequent to the initial processing gained in importance and realization of this resulted in a number of patents for processes whereby the advantages accruing to the use of such accelerators could be gained with at least partial avoidance of scorching troubles. Morton and Harrison¹⁴ superposed plies of compounded rubber containing sulfur and the vulcanization accelerator alternately; in another method of procedure¹⁵ one of two ingredients essential to vulcanization, *e.g.*, sulfur and accelerator, was incorporated in the rubber mix by the customary milling operation, and the other was subsequently applied to the surface of this mix; then penetration by diffusion occurred (conveniently aided by heat), and accelerated vulcanization became possible.

Similar methods for avoiding the scorching troubles experienced in producing ultra-accelerated mixes in the usual manner were described almost simultaneously by Cadwell²; his range of vulcanizing ingredients, however, included organic activating agents as well as ultra-accelerators and was such that vulcanization of the completed mixing could occur even at ordinary temperatures. Moreover, Cadwell made the additional important step of avoiding the use of preformed ultra-accelerators by forming them *in situ* in the rubber when required; a further line of opposition was thus created to scorching or prevulcanization. This development³ was based on the ease of formation of the dithiocarbamate type of ultra-accelerator by the direct spontaneous combination of carbon disulfide and the appropriate amine. By painting the shaped compounded rubber, already containing sulfur, zinc oxide, and the amine, *e.g.*, piperidine, with carbon disulfide, the latter is absorbed; the ultra-accelerator, *e.g.*, piperidine pentamethylenedithiocarbamate, is formed almost at once so that vulcanization occurs spontaneously in a week or so at ordinary temperature or in a shorter time at a higher temperature. At the same time Cadwell and Smith⁵ divided the necessary agents for this type of accelerated vulcanization into four component groups: (1) sulfur or a sulfur-generating material, (2) carbon disulfide or a material generating it, (3) a metal compound, *e.g.*, zinc oxide, and (4) an amine. The omission of at least one of these from a mix would preclude the possibility of prevulcanization; vulcanization could be effected, however, by subsequently incorporating the omitted component by diffusion, *e.g.*, from a solution in benzene. Rubber sheet or a dipped rubber article could, for example, be immersed in a benzene solution of sulfur, zinc butylxanthate and dibenzylamine for a minute or so; after drying, vulcanization could be effected at ordinary temperature in the course of a week or so. The disadvantage in the use of a solvent which is active with the rubber can be avoided by employing an ultra-accelerator dis-

solved in a rubber nonsolvent, such as acetone¹⁶ or even water, or by an emulsion of an ultra-accelerator substantially insoluble in water, such as the carbon disulfide compound derived from the reaction product of piperidine and formaldehyde¹⁸.

At about the same time, the possibility of producing an accelerator of vulcanization *in situ* in the rubber so that a preshaped rubber article could be vulcanized without the need of heat, was also described by Bruni¹. He published a method of cold vulcanization based on compounding the rubber with sulfur, zinc oxide and an aromatic amine, *e.g.*, aniline, and subjecting it to the action of vaporized or dissolved carbon disulfide.

Where prolonged storage of the compounded material is desired, it may be important to exercise still further care in the selection and grouping of the vulcanizing ingredients. For instance, in the preparation of self-vulcanizing doughs for low-temperature repair work by making two mixtures which are to be blended as required, one containing the accelerator, *e.g.*, zinc isopropylxanthogenate, and the other sulfur⁶, the possible presence of traces of free sulfur as an impurity in the xanthate renders it a wise precaution to keep the latter separate from the zinc oxide and to incorporate the zinc oxide in the sulfur stock.

In its various forms the method of vulcanization just indicated not only ensures the avoidance of scorching and secures in the product the physical advantages associated with the use of the best ultra-accelerators, but also gives the possibility of preventing the spoiling of scrap or fresh stock by vulcanization in storage. It also permits the production of sulfur-vulcanized composite articles comprising heat-sensitive components which would be impaired by hot vulcanization in the ordinary way. Furthermore the vulcanization may be effected at the ordinary temperature for which the alternative procedure would be by the use of sulfur chloride with its well-known disadvantages. Admittedly the "diffusion method" of sulfur vulcanization, as it may conveniently be termed, places a limit on the thickness of the article or material to which it may be applied although component sheets may be assembled into composite layers of substantial dimensions.

An interesting application of the diffusion process is in the manufacture of golf balls, where sulfur vulcanization of the outer shell is desired with avoidance of any thermal impairment of the tension of the rubber thread which is wound tightly around the central core. Adaptation of the diffusion method of vulcanization to this particular purpose was indicated almost simultaneously from several sources⁴. There are various possible methods of procedure, but in all of them the manufacture of the ball is taken to the stage of completion of the final molding operation and release of the molds before vulcanization. The last process can be at such a low temperature that, although applied to the freely exposed ball, it does not interfere with the exactness of the detail in the surface pattern. Furthermore, separation of the molding operation from the vulcanization process has other evident advantages.

The form of the diffusion method of vulcanization, in which the article to be vulcanized contains the sulfur, the amine and the zinc oxide for the formation and activation of the ultra-accelerator but lacks the carbon disulfide for the formation of the latter, has the convenience that the carbon disulfide lends itself to a diffusion process of introduction. This introduction may be either from an external atmosphere containing the vapor or from a liquid medium preferably containing the carbon disulfide in admixture (either solution or dispersion) with a nonsolvent for the rubber.

It is of considerable potential importance that carbon disulfide not only provides an essential component for the formation of the ultra-accelerator, but that the activity of the latter is enhanced by the presence of an excess of the carbon disulfide⁸. This effect appears to be analogous to that of zinc oxide on the zinc dialkyldithiocarbamate and zinc xanthate ultra-accelerators¹⁹, and is observed with all such accelerators of the dithio class. For instance, a mixture of smoked sheet rubber 100, sulfur 5, zinc oxide 5, and zinc isopropylxanthate 0.5, becomes well vulcanized when kept for 15 hours at 40° C. in air containing carbon disulfide vapor; it remains quite unvulcanized under similar conditions with carbon disulfide excluded. Zinc diethyldithiocarbamate, piperidinium, pentamethylenedithiocarbamate, the alkylxanthic disulfides, and the thiuram sulfides are similarly influenced.

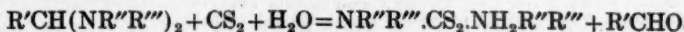
Zinc oxide and carbon disulfide probably both exercised a suppressive action on a tendency of the dithio accelerator (whether formed *in situ* or otherwise) to enter into a by-reaction involving decomposition with formation of these two substances. As with zinc oxide, the additional effect of the surplus carbon disulfide is observed with mixings or doughs in which the preformed accelerators have been incorporated as well as with mixings in which they are formed *in situ*.

According to the principle of delayed-action accelerators, a postponed effect is obtained by incorporating in the vulcanizable mixture a chemical derivative of the accelerator (such as the well-known dinitrophenyl derivative of mercaptobenzothiazole or one of the various acyl derivatives), which undergoes "hydrolysis" at an early stage of the vulcanization period, so that the true accelerator is freed to exert its characteristic action. By analogy with this principle it might be a convenient alternative to the diffusion process to incorporate in the rubber mix a compound capable of liberating carbon disulfide when desired. Unfortunately, although various substances have been mentioned for this purpose, such as the metal thiocarbonates, they do not liberate carbon disulfide with sufficient ease and are disappointing in this respect. Possibly, however, the activation of the dialkyl dithiocarbamate accelerators by the presence of a monoalkyl dithiocarbamate is due, in part at least, to the lower stability of the latter and the ease with which it undergoes decomposition, with formation of carbon disulfide. Incidentally, the use of thiuram disulfides as vulcanizing agents may be regarded, from the point of view of the liberation of free sulfur inside the rubber stock, as the chemical analog of the method of introducing sulfur into the otherwise completed stock by a diffusion process.

In the preparation and use of stocks containing secondary amines for subsequent conversion into dithiocarbamate accelerators by extraneous treatment with carbon disulfide, a number of difficulties may be encountered. The most desirable secondary amines from the point of view of the activity of their dithiocarbamate derivatives as accelerators are liquid at ordinary temperatures; in addition, many of them are distinctly volatile. These features may lead to losses by seepage into the bearings of the mill and by evaporation during mixing and during storage. Rise of temperature during milling may also lead to scorching. With a view to circumventing all these complications, the possibility has been investigated of using the amines in the form of less volatile and solid compounds decomposable by carbon disulfide so that the dithiocarbamate derivative of the amine would still be producible *in situ*. Several classes of compounds which have been tried in this laboratory proved unsuitable. The sulfur dioxide derivatives of the amine, *e.g.*, the piperidine-*N*-sulfinic acid compound obtained from piperidine and sulfur dioxide, are not only undesirably deliquescent but are resistant to

carbon disulfide. The carbon dioxide derivatives, *e.g.*, piperidinium pentamethylenecarbamate and diethylamine diethylcarbamate, are convertible by carbon disulfide into the corresponding dithiocarbamates, but are unfortunately unstable volatile solids and disappear on exposure to the air. The compounds of the amines with the mercaptans proved still less stable, *e.g.*, piperidine evaporated completely from a mixture with octadecyl mercaptan. Two classes of compounds, however, give satisfactory results: (a) the salts of the bases with an organic acid, *e.g.*, with stearic acid or benzoic acid or a mixture of these acids, and (b) the condensation products of amines with aldehydes other than formaldehyde. With the former class of compound incorporated in rubber containing also sulfur and zinc oxide, the extraneous action of carbon disulfide as vapor or as a liquid solution or emulsion causes formation of the dialkylamine dialkyldithiocarbamate (in which term we include also the carbon disulfide derivative of piperidine) with consequent possibility of vulcanization even at ordinary temperatures. The second class of compound comprises a considerable number of substances⁷ obtainable by direct reaction of the dialkylamine, *e.g.*, piperidine, diethylamine, diamylamine, etc., and an aldehyde, *e.g.*, butaldehyde, benzaldehyde, furaldehyde, etc.

The behavior of formaldehyde is different from that of the other aldehydes in that it converts the various amines into their methylene derivatives; and although the latter react with carbon disulfide, they do not regenerate the original amine or form the dithiocarbamate compound corresponding to it. For example, methylenedipiperidine, from formaldehyde and a bimolecular proportion of piperidine, form with carbon disulfide an additive compound, $(C_5H_{10}N)_2CH_2CS_2$, which melts at 58° C.; piperidine pentamethylenedithiocarbamate melts at 174° C. The higher aldehydes and the secondary amines give compounds of the formula $R'CH(NR''R''')_2$ which are decomposable by carbon disulfide according to the equation:



The water naturally present in the rubber mix suffices for the reaction; it is possible by drastic drying, *e.g.*, for a considerable period over phosphorous pentoxide, to prevent the reaction represented by the equation, but such a condition of desiccation is not normal in rubber; for a mixture containing 0.5 per cent of an aldehydeamine compound of molecular weight 250 the proportion of water theoretically required to be present is less than 0.04 per cent. These condensation products of the higher aldehydes and secondary amines are frequently formed spontaneously, and even with heat evolution, when the two components are mixed. It is sometimes convenient to moderate the reaction by diluting one of the reagents with a solvent, *e.g.*, light petroleum, or even to use one or the other in the form of an aqueous suspension. Most of the products are sparingly volatile liquids at ordinary temperatures and so are convenient for handling; others are attractive crystalline solids⁷, *e.g.*, benzylidene dipiperidide, melting at 81° C.

The use of these compounds as an eventual source of the dithiocarbamate ultra-accelerator affords a double degree of protection against scorching. The compounds are less active as accelerators than the corresponding free amines, and the latter are much less active than their dithiocarbamate derivatives. Yet when incorporated in the rubber the former can be converted by the action of carbon disulfide into the corresponding dithiocarbamate accelerators at ordinary temperatures.

In addition to these advantages the vulcanizing activity of the resulting accelerator is further enhanced by application of ammonia gas or an amine after the carbon disulfide treatment or by incorporation of a small proportion of an organic base with the other ingredients in the rubber mix. The presence of the additional substance further expedites the action of the carbon disulfide on the aldehydeamine compound. For convenience of incorporation, the base should be sparingly volatile, and it is important that it should have a fair degree of solubility in the rubber. For this reason diphenylguanidine and di-*o*-tolylguanidine are acceptable, the latter appearing to have a slight advantage with respect to solubility. This matter of solubility in the rubber is the more important because the method just indicated is intended particularly for vulcanization at low temperatures, and it may also be desired to effect compounding with a minimum of temperature rise. This consideration of solubility of the vulcanizing ingredients is much more important here than with ordinary sulfur vulcanization, in which the higher temperature can increase the effectiveness of sparingly soluble ingredients in more than one way.

ACKNOWLEDGMENT

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TEMPERATURE COEFFICIENT OF VULCANIZATION *

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One hundred years ago rubber was the only available substance having the property of long-range elasticity which makes rubber so useful to man. The invention of vulcanization tremendously increased the usefulness of rubber, since it decreased the plastic flow at elevated temperatures and increased the resistance to hardening at low temperatures. It is now the general consensus that vulcanization is caused by a chemical reaction or at least is attended by a chemical reaction. The fact that vulcanization is the result of a chemical reaction is an all-important factor in controlling the nature of the manufacturing processes in the rubber industry. The existence of a temperature coefficient of vulcanization like other chemical reactions exerts a powerful influence on the nature of the manufacturing processes. Thus, vulcanized rubber is made by a thermosetting rather than thermoplastic process.

PRACTICAL SIGNIFICANCE

The manufacture of vulcanized rubber articles and the usefulness of manufactured rubber articles depend, to a large extent, on the existence of a temperature coefficient of vulcanization. Although this is more or less taken for granted, it may be well to enumerate the consequences if vulcanization had no temperature coefficient.

Thus, if the vulcanization of rubber had no temperature coefficient, the chemical reaction causing vulcanization would proceed indefinitely, and rubber compounding, as we know it today, would have to be completely different. For example, the molding and simultaneous vulcanization of rubber articles in commerce would probably have to be done at elevated temperature, as at present, but some means for stopping the reaction would be necessary. Otherwise, the rubber would continue to vulcanize and become unsuitable for use due to overvulcanization. Vulcanization catalysts are called accelerators. If there were no temperature coefficient of vulcanization, not only would accelerators have to be discovered but also anticycatalysts which would stop the vulcanization reaction at the proper stage of vulcanization. Such catalysts would be necessary not only for stopping the vulcanization process at elevated temperatures during the process of molding, but also during the use of the rubber at lower temperatures.

Most of the articles of manufacture which contain rubber are molded and vulcanized at elevated temperatures, since the greater volume of rubber is still consumed by tires and various mechanical goods. The advantage of high temperature in the molding of rubber articles is that the elevated temperature softens unvulcanized rubber so that it will easily take the shape of the mold and also shorten the time of the vulcanization reaction. As a consequence, most of the data on temperature coefficient of vulcanization have been determined from the rate of vulcanization of rubber at elevated temperatures in molds. On the other hand, data on the temperature coefficient of vulcanization in air, steam, ammonia,

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nitrogen and carbon dioxide gases are rarely referred to in the literature, although a considerable quantity of rubber is manufactured under these conditions.

Another important application of the temperature coefficient of vulcanization is that we thus have a means of calculating the time necessary for vulcanization at different temperatures if the rate at one temperature is known. Thus, for some reason, if it is desirable to vulcanize rubber at a different temperature from the one which has been in use for a specific rubber compound, a knowledge of the temperature coefficient of the rate of the vulcanization reaction will permit an estimate to be made of the time necessary for the reaction to take place at the new temperature.

In processing rubber it is undesirable that the vulcanization reaction take place until the manufactured article is in final shape and ready for vulcanization. The fact that vulcanization is a chemical reaction and that it has a normal temperature coefficient, which means a large temperature coefficient, makes it possible to prevent prevulcanization during processing. Thus, one solution to the problem of prevulcanization is merely to keep the rubber cool and therefore cause the rate of vulcanization to be so slow at processing temperatures that no manufacturing difficulties or loss of product is necessary. In industry today the temperatures of processing are sometimes fairly close to the temperatures employed in vulcanization, and this necessitates rapid processing of the rubber or the use of retarders of vulcanization or delayed action accelerators. This adds more complexity to the chemistry of vulcanization, about which little is known from the point of view of the fundamental mechanism.

THEORETICAL SIGNIFICANCE

Rubber manufacturing today is based on sulfur vulcanization. In either soft or hard vulcanized rubber, sulfur combines with rubber during vulcanization. Although other vulcanizing agents are known, none of them is used to a great extent. Empirically the coefficient of vulcanization is defined as follows:

$$(\% \text{ sulfur} / \% \text{ rubber}) \times 100$$

The fundamental knowledge of the character of the combined sulfur compound is not yet complete. In addition, the mechanism or kinetics of the vulcanizing reaction is also highly speculative at present. The rate of combination of sulfur in uncatalyzed vulcanization is usually of zero order. In catalyzed or accelerated vulcanization the rate of combination of sulfur is sometimes first order, but by no means always. Thus, it is not known what the type of reaction is with any degree of certainty. One complicating factor is the high molecular weight of the rubber.

Therefore, the theoretical significance of the temperature coefficient of vulcanization cannot imply much more than to confirm other evidence that the vulcanizing reaction is a chemical reaction.

According to Arrhenius¹ the heat of activation of a one-step chemical reaction can be determined from a knowledge of the temperature coefficient of reaction velocity. If the reaction consists of more than one step, a "heat of activation" can be calculated from the temperature coefficient, but the interpretation is frequently impossible at the present time. In vulcanization we do not know what the steps are; furthermore, there is the possibility that the steps may be different at one stage of the vulcanizing reaction from those at another. It is therefore obvious that very little can be done today in the theoretical interpretation of the

significance of the temperature coefficient of vulcanization. As will be described later, the temperature coefficient equation:

$$\frac{d \ln k}{d \frac{1}{T}} = \frac{\Delta H}{R}$$

is an extremely useful tool in rubber research and practice.

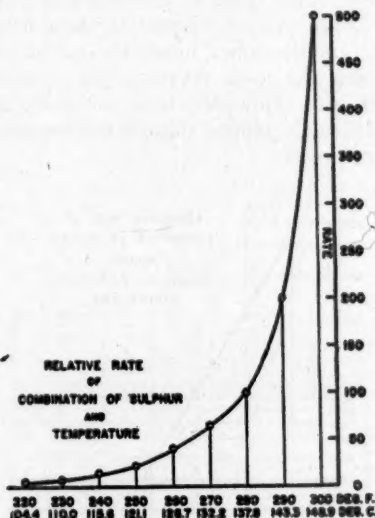


Fig. 1.

TEMPERATURE COEFFICIENT DATA

Since the discovery of the vulcanization of rubber, it has been known that vulcanization proceeded more rapidly at elevated than at lower temperatures because it took less time at the higher temperatures to develop a specific change in physical properties than at lower temperatures. Also, the blooming of the free sulfur to the surface of the vulcanized rubber was an additional criterion.

Vulcanization was put on a chemical basis by Weber¹¹, who first determined combined sulfur as a function of time of vulcanization. The first reliable determination of the temperature coefficient of vulcanization by chemical means was made by Spence and Young¹². In the earlier work there was considerable inaccuracy, due to the fact that the actual temperature of the platens in steam-heated presses in which rubber was vulcanized was not precisely known, although it was precisely controlled and the uniformity of vulcanization was adequate. The technique of analysis of rubber for free and combined sulfur also took years to develop to bring it to a stage where the precision was great enough to determine temperature coefficients.

Historically the experimental methods used for determining the rate of vulcanization at different temperatures have been quite numerous. Many of them have not been reliable for precise work although adequate for the commercial purpose in hand; for example, the maximum tensile strength and the resistance

to swelling have been employed¹⁴ and have undoubtedly been of practical use, although the precision has not been adequate for an accurate determination of the temperature coefficient of vulcanization. The modulus of vulcanized rubber (stress at a specific elongation) increases with time of vulcanization during the early stages of the vulcanization. From such data the rate of the vulcanization may be calculated. Temperature coefficients computed from rates determined from moduli give values for the temperature coefficient which are quite consistent with those determined from combined sulfur and are therefore fairly precise. It has been recommended from a technical point of view that the values determined from moduli are to be preferred to those computed from combined sulfur determinations⁴. On the other hand, the modulus method is subject to the difficulty of choosing the most representative conditions with respect to elongation and state of cure. However, from a strictly scientific point of view the combined sulfur and true combined sulfur⁶ or disappearance of free sulfur are susceptible to greater precision.

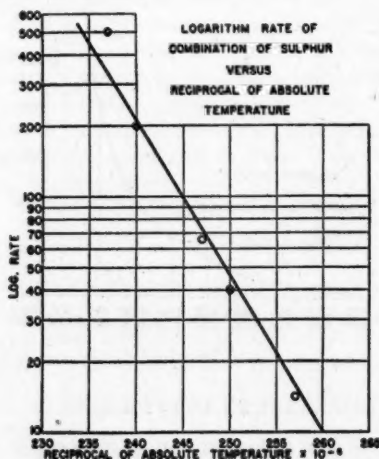


FIG. 2.

The data in the literature on temperature coefficient which have been published since 1930 are summarized in Table I.

The temperature coefficient of the rate of vulcanization ranges from the value 1.87 fold increase in rate per 10° C. increase in temperature to the value 2.67. These values, as given in the literature, depend on the type of accelerator used in the compound as vulcanization catalyst. For example, the unaccelerated compound, rubber (100) + sulfur (6.25), gives the value 2.5; those compounds accelerated with the aldehydeamine accelerators, crotonaldehydeaniline or butyraldehydeaniline, give the values 2.67 or 2.32 and 2.40 or 2.52, respectively; and finally, compounds accelerated with diphenylguanidine, mercaptobenzothiazole or tetramethylthiuram disulfide give values in the neighborhood of 2.00.

The values for mercaptobenzothiazole and benzothiazyl disulfide are identical. This is interesting since the induction period of vulcanization is much greater for benzothiazyl disulfide than mercaptobenzothiazole. Accelerators which exhibit induction periods are called "delayed-action" accelerators. Eliel⁴ drew attention to the observation that the over-all temperature coefficient of vulcanization is

TABLE I
SUMMARY OF TEMPERATURE COEFFICIENT VALUES

Compound	Method	Temp. range ° C.	Temp. coeff.	Citation
Rubber (100) + sulfur (6.25).....	Combined S	135-162	2.5	8
	Modulus	135-162	2.5	8
Mercaptobenzothiazole	Combined S	104-154	2.30	9
	Modulus	104-154	1.91	9
Crotonaldehydeaniline	Combined S	104-154	2.67	9
	Modulus	104-154	2.32	9
Mercaptobenzothiazole	True combined S*	106-152	2.11	7
Mercaptobenzothiazole + diphenylguanidine.....	Modulus	106-152	1.81	7
Benzothiazyl disulfide	True combined S*	106-152	2.07	7
Benzothiazyl disulfide + zinc dimethyldithiocarbamate.....	Modulus	106-152	1.99	7
Mercaptobenzothiazole + diphenylguanidine succinate.....	True combined S*	106-152	1.87	10
	Modulus	106-152	1.87	10
Tetramethylthiuram disulfide	True combined S*	71-154	2.20	10
	Modulus	71-154	1.92	10
Butyraldehydeaniline	True combined S*	71-154	2.40	10
	Modulus	71-154	2.52	10
Mercaptobenzothiazole	Modulus	110-150	2.0	4
Mercaptobenzothiazole + acid salt of diphenylguanidine.....	Modulus	110-150	2.0	4
Dinitrophenylmercaptobenzothiazole + activator.....	Modulus	110-150	2.0	4
Benzoylmercaptobenzothiazole	Modulus	110-150	2.0	4

* Kelley method^a.

numerically the same for accelerators which show pronounced delayed action as for those which show it to a much less extent. He explains this by postulating that the delayed-action accelerators are converted to regulation types by a process involving hydrolysis and that the temperature coefficient of hydrolysis is of the same numerical value as the temperature coefficient of the vulcanization reaction. He adds that the delayed-action effect is a constant proportion of the total time of vulcanization at all temperatures. These deductions, although alluring, are susceptible of experimental proof and have not been proved right or wrong.

The temperature coefficient data in Table I have been determined from modulus (stress at a 500 per cent elongation) or from combined sulfur data. It is worth noting that the temperature coefficient derived from combined sulfur data is in most cases greater than that derived from modulus.

TABLE II

EFFECT OF RECLAIMED RUBBER ON TEMPERATURE COEFFICIENT OF RATE OF VULCANIZATION

Reclaim used	Control	610	682 (acid	672	330
Type of reclaim	Control	(alkali) Whole tire	type) Whole tire	Tread	Red tube
Smoked sheet	100	62.5	62.5	62.5	62.5
Reclaim	—	62.5	62.5	62.5	62.5
Pine tar	2.0	1.25	1.25	1.25	1.25
Zinc oxide ^a	5.0	3.12	3.12	3.12	3.12
Laurex ^b	2.0	1.23	1.23	1.23	1.23
BLE powder ^c	1.0	1.0	1.0	1.0	1.0
BJF ^d	0.60	0.31	0.31	0.31	0.31
Sulfur	3.0	3.0	3.0	3.0	3.0
Temp. coefficient by:					
Free sulfur	2.14	2.51	2.28	2.57	2.28
T-50	2.05	2.50	2.28	2.47	2.19
Modulus	1.88	2.42	2.22	2.34	2.11

^a Kadox Black Label 15 was used.

^b A zinc soap of fatty acids in which lauric acid predominates.

^c An antioxidant prepared from a ketoneamine reaction product.

^d A thiazole derivative of an aldehydeamine.

The fact that the temperature coefficient of rate of vulcanization is approximately equal to 2.0 is evidence that the vulcanization reaction is a chemical reaction.

As stated earlier, no data have been published with reference to vulcanization carried out in air, steam and other gases, or carried out with vulcanization agents other than sulfur, which are suitable for the calculation of the temperature coefficient. There appear to be no published values for temperature coefficient of vulcanization of the synthetic rubberlike materials such as Neoprene, Buna, and Thiokol.

Table II gives data on the effect of reclaimed rubber on the temperature coefficient of rate of vulcanization^a. T-50 values^b and moduli, as well as rate of disappearance of free sulfur, are used in determining the temperature coefficient. All formulas contain approximately 100 parts rubber hydrocarbon on the assumption that the hydrocarbon content for the reclaims is 60 per cent. The concentration of the accelerator was adjusted to give approximately equivalent rates of cure. Less accelerator was necessary in the presence of reclaims because of their activation of accelerators. The temperatures employed were 135°, 140°, 145° and 150° C.

In general, the rubber compounds containing reclaim gave somewhat higher values for temperature coefficient of vulcanization. The values derived from moduli were slightly smaller than those from T-50 or free sulfur determinations.

PRACTICAL APPLICATION

As previously inferred, the practical application of temperature coefficient of vulcanization is the scientific basis for computing the time of vulcanization at some new temperature from data obtained at another specific temperature. This tremendously reduces the amount of experimental data which are necessary in order to establish the proper time for vulcanization at a new temperature.

Some articles of manufacture, such as footwear, are often vulcanized in a large heater in which the temperature is steadily increased during the initial stages of the vulcanization, is held fairly constant during the later stages, and in the final stage is allowed to drop to the final temperature. Were it not for the scientific basis for the temperature coefficient of vulcanization, the computation of the total time of vulcanization in the heater would be completely empirical and very difficult. Since the vulcanization activity can be related to the temperature of vulcanization by proper mathematical relationship, it is possible and extremely useful to compute equivalent times of vulcanization when the temperature of vulcanization is varied during the vulcanization^{2, 11}.

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VULCANIZATION OF RUBBER IN AN ULTRA-HIGH FREQUENCY FIELD *

A PRELIMINARY COMMUNICATION

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THE UNIVERSITY IN THE NAME OF V. M. MOLOTOV, ROSTOV ON DON, U. S. S. R.

There is no doubt about the theoretical interest and the technological significance of the action of ultra-high frequency on high-molecular compounds in general and on raw rubber in particular. The published data available on the effect of high-frequency currents on rubber indicate certain practical advantages and a high speed of "radiovulcanization" compared with the common thermal process. It is claimed that this new method can be applied to rubber articles of considerable thickness.

Preliminary experiments in an investigation of the influence of an alternating electric field of ultra-high frequency on thin films and benzene solutions of rubber have given some positive results.

In the present article no attempt is made to give the underlying theoretical principles and conclusions, since they require further experimental verification. In general, it can be said that ultra-high frequency currents produce not only a thermal effect but have a specific action on the objects under investigation.

EXPERIMENTAL PART

The objects of the investigation were samples of natural rubber (pale crepe) and sodium-butadiene rubber compounded with 5 per cent of zinc oxide and sulfur. The action of the ultra-high frequency field was studied with thin sheets and solutions of the rubbers in benzene (a nonpolar solvent). The solutions were prepared with concentrations of 1, 2 and 3 per cent of rubber. For the preparation of films, solutions containing 5 per cent of natural rubber and 8 per cent of synthetic rubber, respectively, were used. Ten cc. of solution were poured into a crystallizing dish containing some water. A crystallizer of the same capacity, measuring 20 cm. in diam., was used in all experiments. The solvent (benzene) was allowed to evaporate at room temperature, so that a thin film of rubber was formed on the surface. The film was removed and dusted with talc to guard against tackiness. The films were dried in a vacuum desiccator to constant weight and were tested in an ultra-high frequency field. The rubber solutions were poured into glass cylinders with ground-in glass stoppers. The cylinders were suspended parallel with the condenser plates by means of silk threads. The installation of Holburn in the laboratory of K. R. Miram of the Rostov State Medical Institute was used for generating the ultra-high frequency field. The capacity of the generator was 250 watts; the condenser plates measured 5×12 cm. and were set apart a distance of 6 cm.; the field gradient was 450-500 volts per cm. and the wave length was 6 m. (see Figure 1).

In the scheme, L_1 and L_2 are the generator lamps 150; M_1 is the alternating self-induction of the anodic condenser, M_2 of the screen condenser and M_3 of the second condenser; C is the working condenser; R_1 is the lamp generator

* Translated by Charles Blanc for RUBBER CHEMISTRY AND TECHNOLOGY from *Caoutchouc & Rubber* (U. S. S. R.), June 1939, pages 36-37.

of the screen displacement; R_2 is the incandescence rheostat; TP is the incandescence transformer; kV is the kilovoltmeter of anodic voltage; mA is the milliammeter of the anodic current; V is the incandescence voltmeter; $\frac{A}{T}$ is the heat ammeter-indicator.

An idea of the degree of vulcanization can be had from Table I, which gives the analytical data on the determination of free sulfur in rubber solutions and films before and after the treatment with an ultra-high frequency electric field. It also shows the percentage of combined sulfur in relation to the free sulfur before the experiment. The method used in determining free sulfur in all the experiments was to treat the sulfur in the sample with sodium sulfite and determine the resulting sodium thiosulfate by the iodometric method.

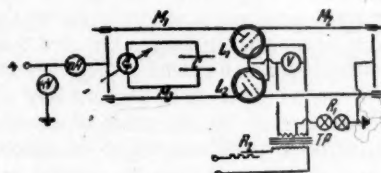


Fig. 1. A basic scheme of a 250-watt generator.

TABLE I

Samples	Percentage free sulfur before the experiment	Percentage of free sulfur after the experiment and percentage of combined sulfur in relation to the original free sulfur			
		After 1 min.	After 5 min.	After 10 min.	After 20 min.
Natural rubber (1% solution)...	3.40	2.50/26.5	2.11/37.9	1.09/67.9	—
Natural rubber (2% solution)...	3.26	1.50/54	1.17/64.1	0.77/76.4	—
Natural rubber (3% solution)...	3.11	2.50/19.6	1.31/57.9	0.50/80.4	—
Synthetic rubber (1% solution)...	1.44	0.74/48.6	0.82/43.1	0.78/45.8	—
Synthetic rubber (2% solution)...	1.51	0.73/51.6	—	0.61/59.6	—
Synthetic rubber (3% solution)...	2.00	1.03/48.5	0.83/58.5	0.37/81.5	—
Natural rubber film.....	3.79	—	3.35/11.6	1.80/52.5	1.72/54.5
Synthetic rubber film.....	3.64	—	2.16/40.7	1.85/49.2	0.98/23.1

CONCLUSIONS

1. Vulcanization of thin sheets and benzene solutions of rubber (natural and synthetic) takes place in an electric field of ultra-high frequency.
2. Vulcanization of rubber in solution proceeds relatively rapidly.
3. Vulcanization proceeds under these conditions relatively fast; the effect of an ultra-high frequency field is manifest after 1 minute.
4. The percentage of combined sulfur increases with increase in the time of action of the ultra-high frequency field.

A THEORY OF ELASTICITY, VISCOSITY AND SWELLING IN POLYMERIC RUBBER-LIKE SUBSTANCES *

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1. INTRODUCTION

The nature of the characteristic elasticity of rubber and other rubber-like substances has been elucidated by Kuhn¹ and Mark², who showed that it is due to the ability of the thread-like molecules of these substances to fold or curl by free rotation of the separate monomeric elements about the single bonds linking them together into a long hydrocarbon chain. A curled form of these thread-like molecules being more probable than an extended one, they must display a tendency to curl simply because of their heat motion, without any actual forces tending to produce such an effect. As a result, an extension of a rubber-like body (without change of volume), entailing a similar average extension of all the molecular chains constituting it in a definite direction, is resisted by an elastic force proportional to the energy of heat agitation, that is, to the absolute temperature.

This situation is quite similar to that which is found in the case of an ideal gas. The pressure exerted by the latter on the walls of the vessel containing it is due, not to a mutual repulsion of the molecules, as was believed long ago, but simply to their heat agitation. The main difference consists in the fact that, instead of a pressure, the heat agitation (free rotation) of the thread-like molecules produces a tension, increasing with the average degree of extension in the given direction. This difference is associated with a difference in the sign of the heating effect produced by a mechanical deformation: whereas a gas is heated on compression and cooled on expansion. In the case of rubber we find an exactly opposite behavior³.

As long as the volume of rubber remains constant, its internal energy can be assumed—as a first approximation at least—to remain constant too, just as in the case of an ideal gas. Introducing the free energy: $F = W - TS$ (where W denotes the energy and S the entropy) we thus see that in both cases the mechanical force f (pressure, tension) corresponding to a given deformation (change of volume, one-sided extension accompanied by a lateral contraction) is determined at a constant temperature, not by the energy, but by the entropy alone, according to the equation:

$$f = T \frac{\partial S}{\partial x} \quad (1)$$

In the case of an ideal gas, the entropy increases with increase of the volume which corresponds to positive pressure; in the case of rubber, on the contrary, it decreases with increase of the extension, which results in a tension.

To obtain a proportionality between f and x , it must be assumed that S is proportional to x^2 (with a negative sign). Accordingly if

$$S = -\frac{1}{2} \alpha x^2 \quad (\alpha > 0) \quad (2)$$

we obtain

$$f = -\alpha T x \quad (2a)$$

* Reprinted from *Acta Physicochimica, U.R.S.S.*, Vol. 9, No. 2, pages 235-250, August 1938.

Equation (2) for the entropy corresponds to an expression of the form:

$$P = Ae^{-\frac{ax^2}{2k}} \quad (A = \text{const.}) \quad (3)$$

for the probability that molecular threads or "chains" are extended in one direction by an amount corresponding to an extension x of the body as a whole. This expression can be derived, and actually has been derived, by Kuhn⁴ for a single molecular thread on the hypothesis of free rotation, or more exactly of random orientation of the consecutive elements of a molecular chain with respect to each other (for a definite value of the valence angle), x denoting in this case the length of the chain in a definite direction, or more exactly of its projection on the positive of the X-axis, x being positive or negative. The coefficient $\frac{k}{a}$ can in this case be defined as the average value of x^2 , whereas the average value of x vanishes (positive and negative values of x being equally probable). We can thus rewrite Equation (3) in the form:

$$P = Ae^{-\frac{x^2}{2\bar{x}^2}} \quad (3a)$$

If $P(x)dx$ is the probability that the length of the molecule along the X-axis lies between x and $x+dx$, and if all values of x between $-\infty$ and $+\infty$ are admitted, although the maximum value of x cannot actually exceed the total length l_{max} of a molecule when fully stretched (this entails but a very small error so long as $x^2 \ll l_{max}^2$), then the value of A is:

$$A = \sqrt{2\pi\bar{x}^2}$$

We shall simplify Kuhn's argument by assuming that the molecule consists of z elements, whose projections on the X-axis can assume two values only, namely either a or $-a$. As a matter of fact one should add to this a zero value at least, but this hardly alters the results. We shall, moreover, identify a with the actual length of one element of the chain, which differs from a by a numerical coefficient of the order of 1.

This amounts to treating the chain as if it were lying parallel to the X-axis, some of its elements being folded over the others, this "folding" replacing the actual "curling". Under such conditions Equation (3a) is a direct corollary of Gauss's error law, the average value of x^2 (determining the width of the Gaussian curve) being given by:

$$\bar{x}^2 = za^2 \quad (3b)$$

The square root of this expression, $a\sqrt{z}$, can be regarded as the average length of the molecules along the X direction—or indeed along any direction—in the normal (unstretched) state of the body under consideration. Since the maximum length of a chain (along X) is equal to za , it follows that the maximum possible extension of the body, measured by the ratio of the maximum length to the normal length (in the unstretched state) is equal to \sqrt{z} . This is an overestimate, for the maximum extension of rubber does not exceed 10, which corresponds to $z=100$, whereas the actual degree of polymerization as measured by z amounts to 10,000 or even to 100,000.

2. VAN DER WAALS FORCES AND THERMAL MOTION

The theory sketched above has been developed by Kuhn and by Mark as if the long-chain molecules of rubber were actually free, the tendency of each of them to curl (or to fold in our simplified scheme) and the resulting elastic pull being absolutely unaltered by the presence of neighboring molecules.

Now it is clear that without a sufficiently strong interaction between the molecules, the stretching of the body constituted by them would produce no elastic reaction whatever. Instead of being stretched by an amount proportional to the macroscopic extension of the body, the molecules would be simply redistributed in space without change of the degree of curling, so that the body would behave as an ordinary liquid, deprived of the characteristic shape-elasticity of rubber-like substances.

The mutual action between the long-chain molecules can be reduced to van der Waals forces acting between their elements. So far as a change of shape of the body, *e. g.*, by extension, is not accompanied by a change of volume, these forces do not produce any work, so that the corresponding potential energy *i. e.*, inner energy of the body, remains constant. They must, however, hold the thread-like molecules together as long as the extension of the body has not surpassed a certain limit corresponding to rupture.

The fundamental difference between the primary valence forces, holding the elements of a chain-like molecule together and the van der Waals forces between the elements of two different molecules, consists, from our point of view, in the fact that, whereas the former correspond to undisruptable bonds between the consecutive elements (allowing them only to rotate between these bonds), the latter give rise to bonds which are more or less easily disrupted by the kinetic energy of the heat motion. This state of affairs can also be described by saying that, whereas the primary valence bonds are permanent as in a solid body (apart from the possibility of free rotation about them), the secondary (van der Waals) bonds are temporary, just as are the bonds between the atoms or molecules in a liquid.

The fact that rubber and other rubber-like substances do not show any fluidity in the temperature range where their characteristic rigidity is displayed must be explained by their extremely high viscosity, in the same way as in the case of ordinary amorphous solids such as glass. This viscosity is the primary effect of van der Waals forces, their influence on the elastic properties being relatively insignificant, just as is the influence of van der Waals forces on the pressure of a real gas.

We shall come back to the discussion of this point in the next section and shall say here a few words about the character of the heat motion of the thread-like molecules as opposed by the van der Waals forces.

A free rotation of the molecule, or rather of its elements about the respective bonds, is of course impossible when this molecule is surrounded by other molecules, whether of the same or a different sort (the latter case refers to the solutions of polymeric substances in ordinary liquids). Instead of free rotations, the elements of a molecular chain must perform rotational oscillations ("hindered rotation") of the same type as in ordinary molecular liquids, that is, oscillations about equilibrium positions (or orientations) which are irregularly changed from time to time, the elementary displacement δ being of the order of 10^{-8} cm., and the average time interval between two such displacements, *i. e.*, on the average duration of a definite equilibrium position, of the order of $\tau = \tau_0 e^{\frac{U}{kT}}$, where

$\tau = 10^{-13}$ sec., is the period of oscillations and U is a certain activation energy which can be considered as a measure of the van der Waals forces.

In addition to these rotation-oscillations corresponding to one degree of freedom per each element of the molecular chain for a fixed value of the valence angle, the heat motion will consist in small oscillations of the $z-1$ angles between the consecutive elements (if z is their number in the chain) and in atomic vibrations within each element, the number of corresponding internal degrees of freedom being equal to $3n - 2 + \frac{1}{z}$ per element if n denotes the number of atoms, constituting it. According to the above picture, the specific heat of a rubber-like substance must be approximately the same as that of a solid body, consisting of the same number of atoms, i. e., $6n$ calories per mole of the monomer constituting the element of a chain. If the rotations of the elements were actually free, the specific heat would be smaller by an amount $\frac{1}{z}$, corresponding to the lack of potential energy in the rotation motion with a fixed value of the valence angle.

3. THE ELASTIC RELAXATION TIME AND THE VISCOSITY OF POLYMERS

We are now in a position to formulate a quantitative theory of the elastic properties of rubber-like substances in a form more general than the purely thermodynamic theory of Kuhn and Mark, making it possible to account not only for the equilibrium relations, but also for some kinetic effects which determine the time necessary for the establishment of equilibrium, the so-called elastic relaxation time τ . In the case of rubber at room-temperature, τ is of the order of 10^{-7} seconds, whereas at the temperature of liquid air it becomes directly observable.

Since the elastic force produced by a piece of rubber or any other rubber-like substance in a stretched state depends on the projection of the lengths of the separate molecules on the direction of stretching, which we shall take for the X -axis and not on the position of their centres of gravity, we shall describe the state of strain by putting one end of each molecule in the same plane: $x=0$, and giving the number $n(x, t)dx$ of molecules whose other end lies (at the time t) at a distance between x and $x+dx$ from it. The ambiguity connected with the possibility of treating either of the two ends of a molecule as fixed in the point (or plane): $x=0$, can be removed by introducing the condition that $n(x, t)$ should be an even function of x in the equilibrium state ($t=\infty$) in the absence of external forces.

The change of the state of strain in the course of time can now be followed by considering the motion of the free ends of the molecules with respect to the fixed ones. Each of these free ends can be treated as an ordinary molecule constituting the terminal monomeric group, which is pulled in the direction of the fixed end by a certain force depending on the distance x . If this force $f_t(x)$ is introduced in a suitable way adequately representing the action produced by the molecular thread on the terminal group, the latter can be dealt with as if it were wholly free, that is, as if there were no "thread" connecting it with the origin at all. In addition to this inner force, an external force of constant magnitude f_0 must be introduced in the general case, representing the effect of the external macroscopic pull applied to the piece of rubber on the assumption that this pull does not give rise to viscous flow because of the extremely high viscosity of the substance, so long as it behaves as a solid body.

The problem of the behavior of the polymer under the above conditions is thus reduced to that of the motion of ordinary molecules (terminal monomers) in a viscous medium under the influence of the thermal or Brownian motion, giving rise to diffusion and of the applied force $f_i + f_e$, producing a convection motion with an average velocity $v = u(f_i + f_e)$ where u is the mobility coefficient. The latter must be connected with the diffusion coefficient D by Einstein's relation $\frac{D}{u} = kT$, holding for ordinary molecules or colloid particles.

The strength of the current formed by the motion of the free ends of polymeric molecules, that is, the number of these ends crossing the plane $x = \text{const.}$ in unit time, is equal to the sum of the diffusion and of the convection currents:

$$j = -D \frac{\partial n}{\partial x} + nu(f_i + f_e) \quad (4)$$

whence the rate of change of the distribution function $n(x, t)$ with the time can be determined from the equation:

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial j}{\partial x} &= 0 \text{ or} \\ \frac{\partial n}{\partial t} &= D \frac{\partial^2 n}{\partial x^2} - u \frac{\partial}{\partial x} [n(f_i + f_e)] \end{aligned} \quad (5)$$

Let us first consider the case of statistical equilibrium, which is specified by the condition $j = 0$. In the absence of an external force ($f_e = 0$) this reduces to

$$D \frac{\partial n}{\partial x} = nuf_i(x)$$

that is,

$$n = \text{const.} \cdot e^{-\frac{u}{D} \int f_i(x) dx}$$

According to Section 1, this function must have the shape of a Gaussian curve with an average breadth za^2 , that is,

$$n = \text{const.} \cdot e^{-\frac{x^2}{2za^2}} \quad (6)$$

whence it follows that

$$f_i = -\frac{D}{2u} \cdot \frac{x}{za^2} \quad (6a)$$

or, since $\frac{D}{u} = kT$,

$$f_i(x) = -\frac{kT}{2za^2} \cdot x \quad (6b)$$

These results cannot be quite exact, since x must not exceed the maximum length of the molecule za , whereas Equation (6) is compatible with any value of x whatsoever. The error introduced in this way, is however, insignificant as long as z is large, for values of $|x|$ far in excess of za are in this case extremely improbable. We are thus entitled to replace $\pm za$ as the limits of x by $\pm \infty$.

With Equation (6a) for the inner force and in the absence of an external force, Equation (5) assumes the form:

$$\frac{\partial n}{\partial t} = D \frac{\partial}{\partial x} \left[\frac{\partial n}{\partial x} + \frac{nx}{2za^2} \right] \quad (7)$$

describing the gradual relaxation of an initially stretched substance. The relaxation time can be estimated in the simplest way, by considering the rate of change of the quantity:

$$\overline{x(t)} = \frac{\int x n dx}{\int n dx} = \text{const.} \int x n dx$$

representing the average extension of the substance at any given moment.

Multiplying Equation 7 by x and integrating with respect to x (between the limits $-\infty$ and $+\infty$), we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} \int x n dx &= D \int x \frac{\partial}{\partial x} \left(\frac{\partial n}{\partial x} + \frac{nx}{2za^2} \right) dx \\ &= D x \left(\frac{\partial n}{\partial x} + \frac{nx}{2za^2} \right) \Big|_{-\infty}^{+\infty} - D \int \left(\frac{\partial n}{\partial x} + \frac{nx}{2za^2} \right) dx \end{aligned}$$

that is, since n and $\frac{\partial n}{\partial x}$ both vanish at the limits of integration,

$$\frac{\partial}{\partial t} \int x n dx = - \frac{D}{2za^2} \int x n dx$$

or finally

$$\frac{d\bar{x}}{dt} = - \frac{1}{\tau} \bar{x} \quad (8)$$

where

$$\tau = \frac{2za^2}{D} \quad (8a)$$

This is a typical relaxation equation, the simple character of the relaxation process being a direct consequence of the linear dependence of the inner force on the distance x . The relaxation time τ turns out to be proportional to the length of the molecules z .

It should be noted that the diffusion coefficient of the terminal monomer D can be expressed in the form $\frac{a^2}{2\tau_1}$, where τ_1 represents (approximately) the relaxation time for such a monomer if it is free to move in the surrounding medium. Hence, it follows that the elastic relaxation time of the polymeric substance under consideration is equal to that of one monomer multiplied by the 4-fold degree of polymerization z .

The relaxation time τ_1 can be defined as the average length of time during which the monomer oscillates about the same equilibrium position before jumping to the next one, and is expressed as a function of temperature by the formula referred to above:

$$\tau_1 = \tau_0 e^{\frac{U}{kT}}$$

where τ_0 is the period of oscillation and U the activation energy for diffusion. We thus find:

$$\tau = 4z\tau_0 e^{\frac{U}{kT}} \quad (8b)$$

If the substance is stretched by an external force corresponding to a certain (constant) value of f_e in Equation (5), we obtain in the same way as before:

$$\frac{\partial}{\partial t} \int x n dx = - \frac{D}{2za^2} \int x n dx + u f_e \int n dx$$

that is,

$$\frac{d}{dt} \bar{x} = - \frac{1}{\tau} \bar{x} + u f_e \quad (9)$$

whence, with $\bar{x}=0$ for $t=0$

$$\bar{x} = \tau u f_e \left(1 - e^{-\frac{t}{\tau}} \right) \quad (9a)$$

$\tau u f_e$ being the equilibrium extension. Inserting Equation (8a) for τ , we for this equilibrium extension the value:

$$\bar{x}_\infty = \frac{2a^2 u}{D} z f_e$$

which, according to Equation (6a), corresponds to an equilibrium between the external force and the average internal force.

It seems natural to identify the elastic relaxation time with the relaxation time τ , characteristic of the hydrodynamic viscosity of the substance.

Since the specific viscosity coefficient η can be represented as the product of the modulus of rigidity, which is practically independent of z , and the relaxation time, we see that on the above assumption η must vary linearly with z , which is in agreement with the empirical formula of Staudinger⁵.

I hope to come back to this question in a subsequent paper.

4. THE MECHANISM OF SWELLING

Highly polymeric substances in the solid state are distinguished from ordinary solids by their capability of absorbing large quantities of certain simple liquids and increasing their volume without any change of shape.

In some cases this swelling is practically limitless and is accompanied or concluded by a dissolution of the polymer in the liquid. In other cases the polymers are characterized by a certain limited extent of swelling, amounting sometimes to a hundred-fold increase of volume, without marked variation of hardness and elasticity.

As has been shown by Staudinger⁵, the limited swelling capacity is due to the presence of an extremely small amount of some substance (also polymeric, as vinyl acetate for example, in the case of polystyrenes) which sews the separate thread-like molecules of the polymer together. This effect is in principle similar to vulcanization but differs from the latter by the fact that the elastic properties of the body remain practically unaffected by the addition of the linking substance, obviously because of its negligible amount.

It is generally believed that the swelling of a polymer through the adsorption of some liquid "filler" is due to the attraction of the small molecules of the

latter by the huge molecules of the former. From this point of view, swelling is a process similar to capillary adsorption, and must be characterized thermodynamically by a decrease of internal energy of the system, owing to the solvation of the macromolecules of the polymer by the micromolecules of the filler.

I wish to advance here the alternative view that swelling is fundamentally a process of osmotic character, due not to potential but to kinetic forces, that is, to heat motion of the molecules of the filler, and connected not with a decrease of energy but with an increase of entropy, just as in the case of spontaneous contraction of a stretched piece of rubber after the removal of the external force (Section 1)⁶.

The surface of the polymer plays the same role in the process of swelling as a semipermeable membrane in ordinary osmosis, the thread-like molecules of the body lying at or emerging on its surface being more or less firmly held together but presenting no obstacle to penetration of the molecules of the "filler". Of course this penetration can take place on the condition only that there is a certain attraction between the two kinds of molecules; a substance can act as a filler of a given polymer, only if the latter is wetted by it. Thus rubber, which is "waterproof" cannot swell in water. This circumstance does not, however, invalidate the principle stated above that the process of swelling is fundamentally determined, not by these forces, but by kinetic forces causing diffusion of the molecules of the filler inside the polymeric substance.

The situation is here quite similar to that which is met with in Kuhn and Mark's theory of the elastic properties of rubber, although these properties could not be displayed without the action of the van der Waals forces holding the thread-like molecules of the polymer together; yet the elastic stress is produced not by these forces but by kinetic forces connected with the thermal agitation of the molecular threads.

The kinetic theory of swelling is supported by a consideration of the thermal effect accompanying this process in conjunction with the vapor pressure of the filler absorbed by the polymer in equilibrium with the latter. Just as in the case of ordinary solutions, this vapor pressure is decreased with respect to the pure solvent (filler) by an amount which tends to zero with increased swelling.

It has been shown by Katz⁷ that the difference between the free energies of the filler in the free and in the bound state calculated from the equation:

$$\Delta F = RT \log \frac{p_0}{p} \quad (10)$$

where p_0 is the vapor pressure of the pure filler and p that of the bound one, is almost exactly equal to the amount of heat absorbed in the process of swelling at a constant temperature T . This coincidence is considered by Katz as a proof of the fact that swelling is connected with a decrease of potential (internal) energy and consequently has nothing to do with diffusion.

This argument is certainly a misunderstanding. In fact the above coincidence established by Katz experimentally must be considered as proof of the converse statement, namely, that swelling is fundamentally a diffusion process, which is associated with no substantial change of internal energy, and can be characterized by an increase of entropy (the heat absorbed being equal to the product of this increase and temperature T).

The vapor pressure of the bound filler closely approaches that of the free one when it is introduced into the polymer in quite insignificant amounts, a few *e. g.*, 1-3, per cent by weight. This fact can be interpreted in a somewhat

paradoxical way, by considering the polymer containing this small amount of the filling substance, not as a solution of the latter in the former, but on the contrary as a solution of the former in the latter. If we take into account the fact that the molecular weight of the polymer is many thousand times (10^4 - 10^5) larger than that of the filler, we see that the introduction even of one gram of the latter into 100 grams of the polymer leads to a solution of the polymer in the filler with a very small molecular concentration, amounting to 1 molecule of the polymer per 100 or even 1000 molecules of the filler. We are thus entitled to apply to such a system the laws referring to dilute solutions, and in particular Raoult's law of the decrease of the vapor pressure:

$$\frac{p_0 - p}{p_0} = \frac{N}{N'}$$

where N and N' denote the numbers of molecules of the polymer and filler, respectively ($N \ll N'$).

I have not yet been able to compare this formula with the experimental data accurately; but it is at least in qualitative agreement with them so far as the order of magnitude of $\frac{\Delta p}{p_0}$ is concerned for a swelling exceeding a few volume percent, as well as its rate of change with increasing swelling (the relative increase of volume being approximately the same as the relative increase in weight).

As a second application of the laws of dilute solutions, we shall consider the maximum swelling of a polymer as determined by the condition of equilibrium between the osmotic pressure of the dissolved substance, *i. e.*, of the polymeric molecules, and the elastic stress due to the increase of volume. It should be noted that in the absence of a filler, a change in the volume of a polymeric substance, whether by extension or by compression, would be connected with a manifestation of ordinary elastic forces corresponding to a change of the mutual potential energy of the molecules and characterized by a very high value of the modulus of elasticity of the same order of magnitude as for an ordinary substance, *e. g.*, 10^5 kg. per sq. cm. In the presence of the filler these forces are not called into play, the elastic stress produced by the swelling being determined by the same relatively small elasticity modulus E (of the order of 10 kg. per cm.) which is effective in the extension of the polymer without change of volume. If the osmotic pressure is calculated according to van't Hoff's law, we obtain, as the equilibrium condition, the equation:

$$E \frac{v - v_0}{v_0} = kT \frac{N}{v} \quad (11)$$

where v is the actual volume, and v_0 the volume of the "dry" substance in the absence of the filler. The maximum swelling $\alpha = \frac{v}{v_0}$ is thus determined by the equation:

$$\alpha(\alpha - 1) = \frac{kTN}{Ev_0} \quad (11a)$$

The expression $\frac{kTN}{v_0}$ is equal to the pressure which the molecules of the polymer could exert if they formed an ideal gas with the same concentration as that of the "dry" substance. For an ordinary substance with a concentration

corresponding to the liquid or solid state, this pressure would amount to a few thousand atmospheres (at room temperatures). For a polymeric substance with $z=10^4$, it would be about 10^4 times smaller, that is, of the same order of magnitude as E (a few atmospheres). The right side of Equation (11a) thus turns out to be of the order of unity, which makes x relatively small, *e. g.*, of the order of a few units.

In reality this figure can often be greatly exceeded, values of x amounting to 100 and even more being observed with insoluble polystyrenes⁵.

We thus see that the above theory requires certain amendments, which amount to an increase of the osmotic pressure compared with the value given by van't Hoff's law. This is natural, for although van't Hoff's law holds for extremely dilute solutions irrespective of the shape and size of the dissolved molecules or colloid particles, yet its applicability in the present case, taking into account the interweaving of the molecules and the presence of lateral links between them, although in a very small number, just sufficient to prevent their dissolution, appears somewhat dubious.

According to Kuhn's theory¹, the elasticity modulus of a rubber-like substance, corresponding to one-sided extension, accompanied by a lateral contraction which leaves the volume unchanged, is equal to:

$$E = 7 \frac{kTN}{v_0} \quad (11b)$$

which leads to:

$$\alpha(\alpha - 1) = \frac{1}{7}$$

that is:

$$\alpha - 1 \cong \frac{1}{7}$$

This figure could be raised a little by taking into account the difference between the modulus of elasticity for a one-sided extension and that for a volume extension with which we are here concerned. It does not seem worth while, however, to dwell on these minor details in view of the obvious fallacy of the theory in the description of the major factor (osmotic pressure). The interesting point which we should like to note in connection with Equation (11a) is the fact that the elasticity modulus of the kinetic theory of Kuhn and Mark must depend on the temperature and the concentration $\left(\frac{N}{v_0}\right)$ in a way quite similar to that which is characteristic of the osmotic pressure, so that the maximum swelling α , as determined by Equation (11a), should be independent both of the temperature T and the degree of polymerization z (which determines the number of molecules N). This latter conclusion is, however, certainly wrong, for the maximum swelling capacity of a polymer is known to increase with the degree of polymerization.

A very high degree of swelling, *e. g.*, above 100-fold, substantially alters the mechanical properties of the polymer, which becomes a gel-like substance. This is simply explained by a decrease of the viscosity coefficient. As long as the latter remains large enough, the gel behaves as a body possessing rigidity, capable of resisting the action of external forces which tend to alter its shape. This gives the key to an understanding of the mechanical properties of lyophilic gels if they are considered as highly swollen polymers consisting of long-chain

molecules, with a relatively small number of lateral links. It is well known that silica gels can be obtained with a dilution of the substance in a volume of water 100 times as large. A full understanding of their mechanical properties is reduced to a consideration of the question as to the variation of the viscosity coefficient with dilution.

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- ² Guth and Mark, *Naturwissenschaften* **25**, 353 (1937).
- ³ It should be kept in mind that the analogy is not complete, because in the case of rubber an extension is accompanied by a lateral contraction corresponding to a constancy of the volume.
- ⁴ Kuhn, *Kolloid-Z.* **68**, 2 (1934).
- ⁵ Staudinger, *Trans. Faraday Soc.* **32**, 323 (1936).
- ⁶ Note added in proof. —After this paper had been sent to press I found that similar ideas with respect to swelling had been expressed much earlier by Haller (*Kolloid-Z.* **56**, 262 (1931)).
- ⁷ Katz, "Röntgenographie der Zellulose", 1934.

COLLOIDAL STRUCTURE OF RUBBER IN SOLUTION

COLLOIDAL ASPECTS OF VULCANIZATION *

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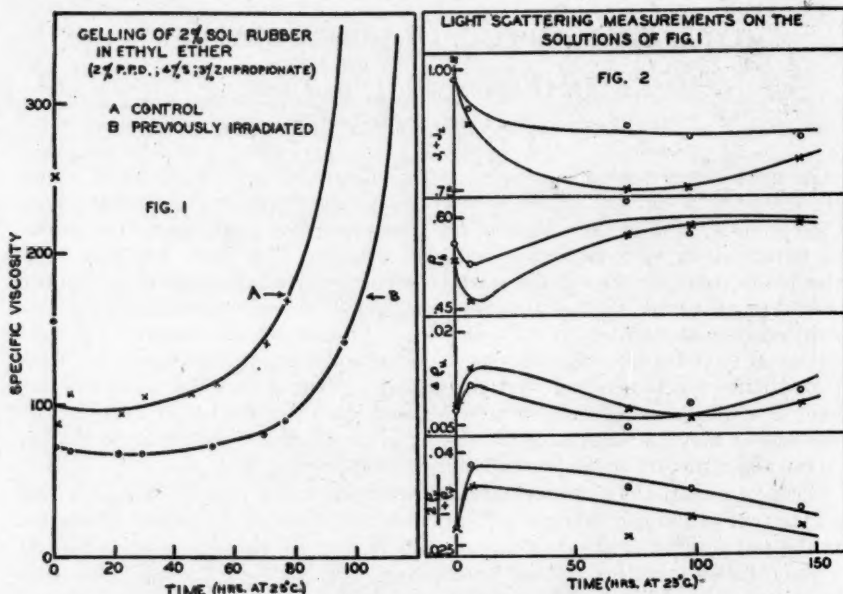
The work here reported is a continuation of studies^{8, 9} on the colloidal structure of rubber in solution, by means of viscosity measurements and measurements of the intensity and depolarization of the transversely scattered light. The previous papers dealt with reversible colloidal changes. The work has now been extended to cover the irreversible changes which occur when a solution of rubber is gelled or vulcanized by a system of curing agents—namely, piperidinium pentamethylenedithiocarbamate (P. P. D.), zinc propionate and sulfur. The advantage of studying the colloidal aspects of vulcanization in solution rather than in solid cures lies in the fact that the colloidal changes are more accessible for direct observation in solution. In a gelled solution, the colloidal structure of the solid rubber may be thought of as existing in an expanded condition, so that in a sense the structure under examination is magnified.

Chemical explanations of vulcanization restricted to the rate of sulfur addition and the type of sulfur bonding^{3, 11, 19} cannot be expected by themselves to account for the physical properties of the vulcanizates because these properties depend on the colloidal structure formed during vulcanization. Van Rossem¹⁴ discussed the status of theories of vulcanization and emphasized that a chemical theory should regard vulcanization as a type of polymerization in which a three-dimensional network of primary valence linkages is built up between large molecules. Such a structure is essentially colloidal in nature, but van Rossem restricted the use of the word to theories of vulcanization in which soft vulcanized rubber is regarded as a colloidal dispersion of hard rubber. In a broader sense than this greatly restricted historical usage, the vulcanization of rubber should be regarded as a colloidal process initiated by chemical reactions. Furthermore, it appears that the amount of chemical action, by which is meant change in primary valence linkages, required to produce the colloidal changes and affect the physical properties is small^{4, 17}. Presumably a single cross-linkage can tie together more or less effectively entire colloidal units or clusters of molecules instead of just single large molecules, as van Rossem considered the structure to be. The importance of paying more attention to the colloidal aspects of the situation thus becomes apparent.

The colloidal nature of the process of vulcanization has not been entirely ignored in fundamental work on vulcanization. Williams¹⁸ made a detailed study of colloidal phenomena in gels of lightly vulcanized rubber. Many instances of vulcanization in solution are reported in the literature. Vulcanization with solutions of sulfur chloride was studied by Garvey⁷ and earlier workers. Garvey's suggestion that a change occurs in the *cis-trans* relations of the units in the long-chain molecules on vulcanization with sulfur chloride is not consistent with x-ray diffraction results. Boiry¹ investigated the gelling of rubber solutions by

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means of sulfur and the application of heat. The action of ultra-accelerators in rubber solutions has been reported on by Thiollet¹⁶ and by Bourbon², whose work includes results with a variety of solvents.



APPARATUS AND METHODS

The light scattering measurements were made with apparatus previously described^{8, 9}. To prepare the solutions, the curing ingredients were dissolved in sodium-distilled ethyl ether, which was also used as the rubber solvent. The solution of the curing agents was filtered into the tube of the light-scattering cell. The intensity of the light scattering from such a filtered solution was found to be negligible in comparison with the intensity from the rubber solutions. The desired amount of rubber, purified by diffusion in petroleum ether, was weighed and introduced into the bulb of the cell. The cell was then evacuated and sealed off. The solvent was distilled onto the rubber, and when the solution was complete, light-scattering measurements were made. The curing ingredients, which were left in the tube by the distillation, were then dissolved in the rubber solution by pouring the solution into the tube. Light-scattering and viscosity measurements were made at suitable intervals. By this technique any exposure of the rubber solution to air was avoided. The cell was kept in the dark, and when viscosity measurements were being made, it was protected by a wrapping of red Pliofilm.

In the experiments where viscosity but not light-scattering measurements were made, solutions of milled crepe rubber were used. The rubber was prepared by milling pale crepe rubber so that a one per cent solution in benzene gave a specific viscosity of 6.07. Baker's C. P. benzene was used as the solvent in these experiments.

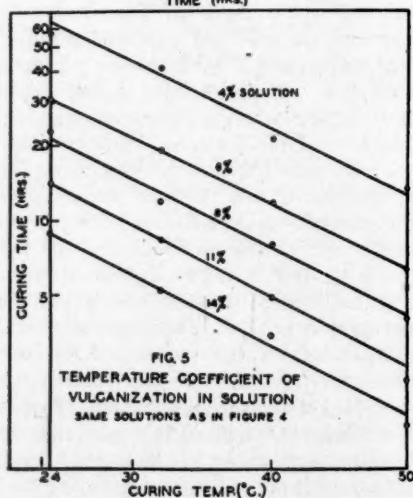
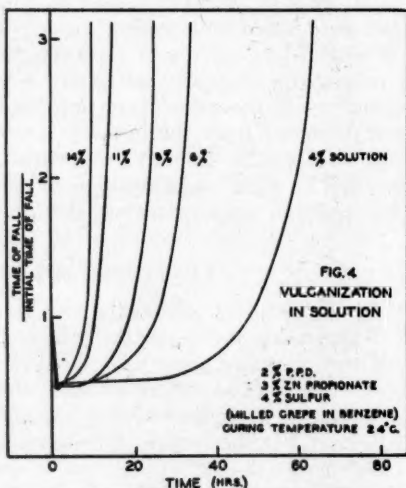
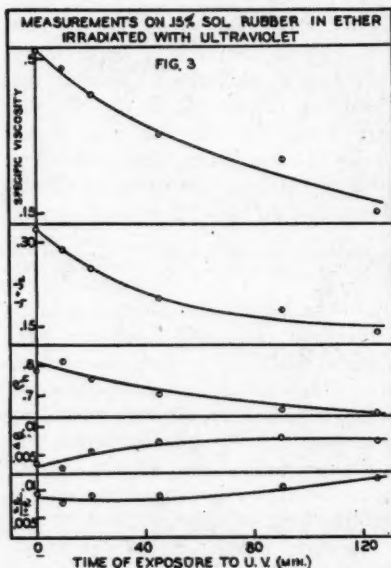
The milled pale crepe rubber was dissolved in benzene to give a 14 per cent solution by volume. Portions were diluted when lower concentrations were required. In carrying out the experiments, glass tubes (15 mm. inside diameter and 30 cm. long) were filled with solutions of the desired concentrations. The curing ingredients were weighed out on an analytical balance and stirred into the solutions with a glass rod. Viscosity measurements were made by timing the fall between marks of a steel ball of suitable diameter, usually $\frac{1}{16}$ inch. The tubes were closed with rubber stoppers protected by aluminum foil but the ball was returned to the top of the tube with a magnet so that it was unnecessary to remove the stoppers and insert a ball for each measurement. During the measurements the tubes were immersed in a water thermostat at 30° C. and were protected from the light by a wrapping of red Pliofilm. At other times they were kept in the dark. For cures at various temperatures, the tubes were immersed in water thermostats or in uniform-temperature ovens with circulating air so that the temperature was uniform and constant to about $\pm 0.25^\circ$ C.

LIGHT SCATTERING MEASUREMENTS

The theory which relates the size and shape of colloidal light scattering units to the intensity and depolarization of the transversely scattered beam was outlined in a previous paper⁸. Reference should also be made to more recent articles^{10, 12, 13} for the present status of the theory. Lotmar made general criticisms of the type of equipment used by the authors as subject to error due to secondary scattering. For the systems investigated, the intensity of the light scattering was so low that we do not believe it was a source of appreciable error. Figure 1 shows the viscosity changes for 2 per cent solutions of sol rubber in ethyl ether due to the addition of 2 per cent piperidinium pentamethylenedithiocarbamate, 4 per cent sulfur, and 3 per cent zinc propionate. For curve *B* the solution was irradiated with ultraviolet light before the curing ingredients were added. Figure 2 gives light-scattering measurements on the same solutions. The curves for the intensity of the scattered light and the depolarization factors, ρ_\perp and $\Delta\rho_\perp$, consistently indicate that the initial drop in viscosity is accompanied by an increase in the size of the colloidal units. At first thought this may seem contrary to the generally accepted idea of a prevulcanization disaggregation. The origin of this conception is undoubtedly the intuitive reasoning that the strength and elasticity of rubber are associated with the molecular structure of a solid, and that as rubber becomes weaker and more plastic, the continuous structure of the solid is broken. There is no contradiction between this fundamental line of thought and an observation that the colloidal units become larger in the process of disaggregation. As a crude analogy, a block of concrete may be taken as an example. The aggregates in the block are the pieces of gravel. The block may be disaggregated in such a way that cement will adhere to the gravel and the resulting aggregates will be larger than before. By the prevulcanization disaggregation must be understood a weakening of the continuous structure or "interlocking" of the colloidal units in the rubber and not a decrease in their size.

This interpretation of the light-scattering measurements and the resultant concept of the disaggregation is in contradiction to the ideas of Staudinger¹⁵, who regarded the viscosity of a rubber solution as due to individual, long, threadlike molecules. For such a structure any decrease in viscosity must of necessity mean a decrease in the size of the colloidal units which are considered to be the individual macromolecules. In opposition to this, the light-scattering measurements show that the effects which have been observed and attributed to a pre-

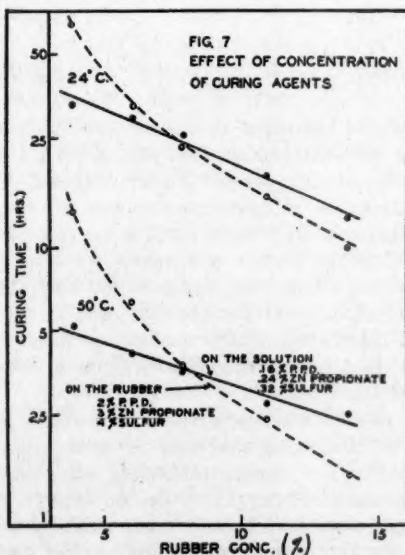
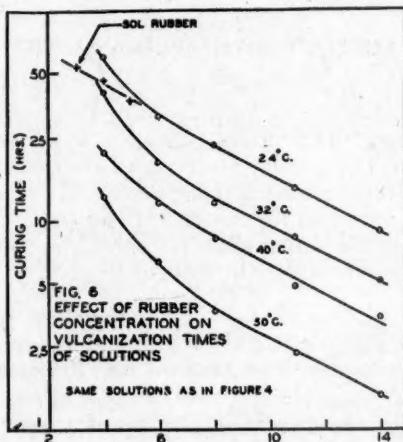
vulcanization disaggregation are due to a growth in particle size carried out in such a way that interlocking of the colloidal units is diminished. The degree and amount of interlocking may reasonably be a more important factor in determining viscosity and plasticity than the size of the units. It is easy to visualize a growth in particle size, even for a solution of macromolecules such as postulated



by Staudinger, which would lead to a decrease in viscosity. Thus, if the individual molecules align themselves in parallel groups, from simple mechanical considerations the resistance to flow should decrease.

Comparison of the curves of Figure 2 with those of Figure 1 shows that colloidal changes are occurring while the viscosity is constant and that the viscosity is by no means a complete specification of the colloidal structure. This constant viscosity must therefore represent an equilibrium condition between the colloidal

processes of disaggregation and those which later cause gelation. The curves of Figure 3 have a bearing on this subject. They represent measurements on a dilute solution of sol rubber irradiated with ultraviolet light in the absence of air. The course of the light-scattering curves is similar to those of Figure 2 during the early stages of vulcanization. Although the light-scattering measure-



ments indicate a close similarity between disaggregation caused by irradiation and the initial disaggregation caused by the vulcanizing ingredients, the previous irradiation has the effect of delaying vulcanization, as Figure 1 showed. This is evidence that the early stages of vulcanization represent not merely a disaggregation but an equilibrium between the disaggregating and gelling processes from the start.

More evidence for this view is given in Table I. The accelerator, accelerator-sulfur and accelerator-activator were added to benzene solutions of crepe rubber. After standing for 17 hours, the time required for gelation to start when the whole curing formula was added at once, the ingredients missing from the complete formula were added to the respective tubes. A comparatively long time was required in each case for gelation to occur.

TEMPERATURE COEFFICIENT OF VULCANIZATION IN SOLUTION

The curves of Figure 4 show that after the viscosity starts to increase, it rises with extreme rapidity so that relative curing times can be defined in terms of the viscosity changes. This makes possible a more accurate experimental measurement than would be possible by trying to observe times of gelation. The time for vulcanization for this work is therefore defined as the time required after the curing ingredients are added for the original viscosity of a solution to increase by a factor of 2. All of the curing times plotted in subsequent figures were obtained from viscosity curves similar to those of Figure 4.

TABLE I
TEN PER CENT SOLUTIONS OF MILLED CREPE RUBBER IN BENZENE

P. P. D. %	Originally added		Added after 17 hr.		Total time for gelation hours
	Zn pro- pionate %	Sulfur %	Zn pro- pionate %	Sulfur %	
2	3	4	—	—	17
2	—	—	3	4	34
2	3	—	—	4	345
2	—	4	3	—	102

Figure 5 is a plot of the logarithm of curing time against temperature. The temperature coefficient of vulcanization is defined as the ratio of the curing times for a 10° C. temperature interval. Figure 5 shows that this coefficient is practically independent of the rubber concentration for the range investigated, 4 to 14 per cent concentration. Its value for the 8 per cent solution is 1.91 per 10° C. In a summary of the results of various workers on solid cures Eliel⁶ gives values ranging from 2.52 to 1.82, based on modulus and depending on the accelerator used. The value found for the solutions is thus very close to the values for solid stocks. This gives confidence that a study of the gelation of the solutions is a valid method for making fundamental investigations on the colloidal nature of vulcanization.

Figure 6 shows that a linear relation exists, except at the lower concentrations, between the logarithm of the curing time and the concentration of the solutions. Three points are given for low concentrations of sol rubber in benzene using the same vulcanizing system. These points lie on the extension of the straight line for the milled crepe solution. The solutions of sol rubber had much greater viscosities than corresponding solutions of milled crepe rubber. The rapid increase in the time of cure at lower concentrations may therefore be partly due to the thermal agitation of the colloidal units which makes it difficult to build up a gel structure. This idea is also supported by the fact that for 50° C., the linear relation begins to fail at 8 per cent concentration, but at 24° C. it extends to 6 per cent. The curing time is related in a simpler way to the concentration of rubber than it is to the initial viscosities of the solutions. From this it fol-

lows that the chemical reaction with the hydrocarbon is more of a controlling factor for the time of cure than the initial colloidal condition.

Figure 7 shows that when the concentration of curing ingredients per cubic centimeter of solution is maintained constant and the concentration of rubber varied, the plot of the logarithm of the curing time against the rubber concentration is a straight line over the range investigated. The dashed curves are taken from Figure 6 for comparison.

The fact that the use of a higher concentration of curing agents in the solution extends this linear relationship to lower rubber concentrations casts some doubt on the adequacy of thermal agitation as an explanation for the long curing times for dilute solutions. At any rate, the controlling factor could not be the thermal agitation in the rubber solution before the curing agents are added.

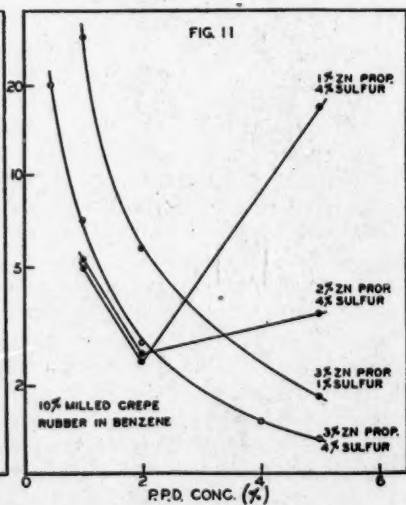
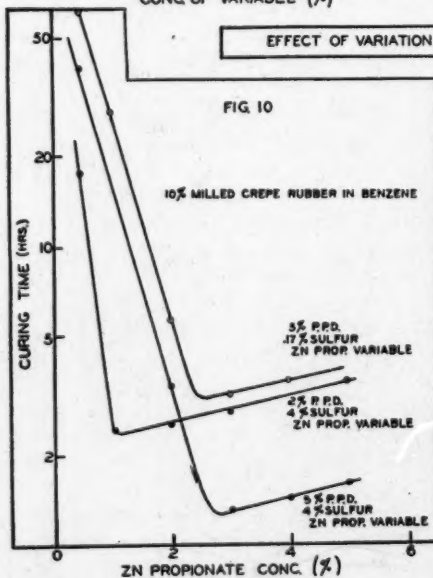
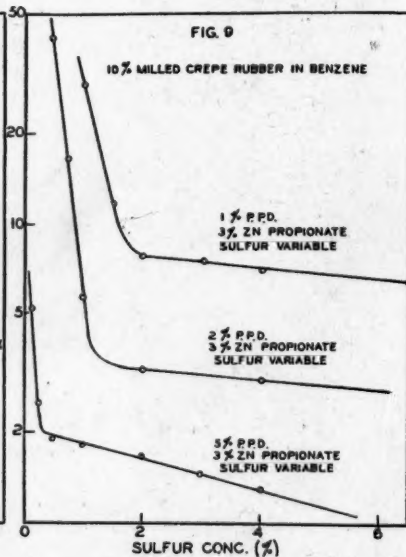
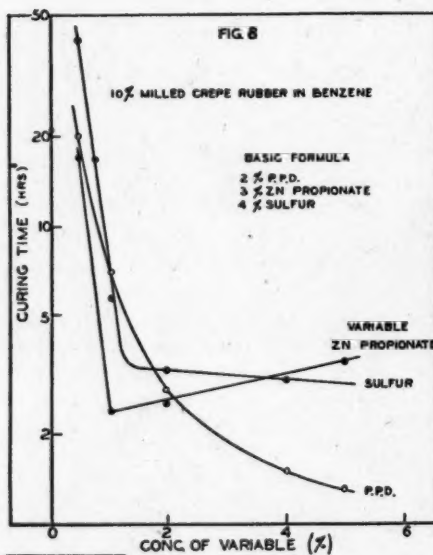
As an analogy to the temperature coefficient of vulcanization it is possible to define a concentration coefficient of vulcanization for these solutions. This may be taken as the ratio of the times required to cure solutions which differ by one per cent in rubber concentration. This is approximately independent of the temperature. For the linear portion of the curves of Figure 6, this coefficient is 1.16; for the solid curves of Figure 7 it is 1.10.

A complete description of the effect on the curing time of variations in a formula containing three ingredients (accelerator, sulfur and activator) would require a system of surfaces in space for graphical representation. The curves of Figure 8 show the effects when one ingredient in the formula 2 per cent piperidinium pentamethylenedithiocarbamate, 3 per cent zinc propionate and 4 per cent sulfur is held constant and the other two are varied. If the percentage of sulfur exceeds 1.5, further increase has small effect on the curing time. The curing times with zinc propionate variable show a minimum. Increase in accelerator content, however, decreases the curing time continuously for the range studied.

Figure 9 gives curves for which the zinc propionate was held constant at 3 per cent. These curves do not favor the idea of a reaction between sulfur and accelerator as a controlling factor for the time of vulcanization, since the break in the curves is shifted to a lower sulfur content as the accelerator content increases.

The curves of Figure 10, in which the break is shifted to lower zinc propionate values as the piperidinium pentamethylenedithiocarbamate is decreased, may be interpreted as showing that a higher zinc content is required to make the higher accelerator content effective in reducing the time of cure. This hints of a reaction between piperidinium pentamethylenedithiocarbamate and zinc propionate. There is also evidence for such a reaction from rubber compounding data⁵. It is curious that an excess of zinc propionate actually retards the cure. The curves in Figure 11 bear out the above interpretations in a general way. If the zinc content is low, a high piperidinium pentamethylenedithiocarbamate content can actually retard the gelation. This may be attributed to the colloidal effect on the hydrocarbon of the excess of the accelerator.

Without meaning to suggest that the above results can be generalized to other curing systems, the data favor the idea that there is a reaction between the zinc salt and piperidinium pentamethylenedithiocarbamate rather than between piperidinium pentamethylenedithiocarbamate and the sulfur. The difficulty in applying the theory of reaction rates is apparent when it is realized that vulcanization results from a complicated series of reactions, the final step of which should probably be considered as a catalyzed polymerization. The intimate connection of these chemical and colloidal changes is most clearly demonstrated by such studies of vulcanization in solution.



SUMMARY

Colloidal changes in solutions of purified rubber due to a vulcanizing system consisting of piperidinium pentamethylenedithiocarbamate, sulfur, and zinc propionate have been followed by means of measurements of the depolarization and intensity of the transversely scattered light and by viscosity measurements.

A study was made of the time required for vulcanization of benzene solutions of rubber with the above vulcanizing agents. The temperature coefficient of vulcanization was approximately the same as that for cures of solid stocks.

The light scattering results are interpreted as showing that, upon the addition of the vulcanizing agents to the solutions, the colloidal units become larger. The decrease in viscosity is explained as being due to a diminished "interlocking" of the units. In the vulcanization of the solutions, an equilibrium of colloidal processes occurs which results in a constant viscosity for the larger part of the time required for vulcanization, although the light scattering measurements show a continuous change. The magnitude of the light scattering changes indicates that the molecular clusters in the gelled solution are probably not very different from those in the original solution. The viscosity measurements show that the forces between the clusters have been radically strengthened.

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MACROMOLECULAR COMPOUNDS

CCXVI. DETERMINATION OF THE LATTICE OF RUBBER *

E. SAUTER

In an earlier work¹ a rotating crystal diagram, three different Schiebold-Sauter (rotating goniometer) equatorial diagrams and two different photomicrographs of the same sample of a single crystal were described and shown to be conclusive proof of the single-crystal texture of the sample under examination. If, in their work on the same subject, Meyer and Mark² had likewise taken numerous photographs of different kinds, instead of a single photographic film, a comparison of the various photographs would speak for itself. In taking his rotating crystal goniometric photographs, the present author used uniformly thick, frozen small cubes of rubber, the intensities in the reflections of which were the same in all directions. On the contrary, in the photographs of Meyer and Mark, a stretched film of rubber, which reflected considerably less uniformly than did the samples used by the present author, was photographed at rest and therefore without being rotated. Although Meyer and Mark agree to the interference 300, they maintain that this does not explain in any way the appearance of reflection A_2 .

If Meyer and Mark had gone to the trouble of taking the same kind of photographs as those of the present author, which were obtained by a reliable x-ray method, they would have obtained different results from those they actually did obtain. Meantime, Morss³, wholly independent of the present author, proved that both in the lattice determination of Mark and von Susich⁴ and in that of Meyer and Lotmar⁵ disagreements occur between certain observed and calculated reflections, which are greater than the possible errors in the measurements. Morss therefore came to the same conclusion as the present author, *viz.*, that no part of the lattice of Meyer and Mark is correct. Morss then derived two new unit cells of crystalline rubber, which he attempted to distinguish. It may be assumed that similar relations exist between these two lattices of Morss as have earlier been found in the case of the double indices of natural and hydrated cellulose. Cell I of Morss has the constants: $a=26.3$ A.U., $b=8.15$ A.U., $c=8.9$ A.U. and $\alpha=109^\circ 30'$. Cell II of Morss is orthorhombic and has the lattice constants: $a=12.4$ A.U., $b=8.15$ A.U. (fibre axis), $c=8.9$ A.U. For a comparison, the lattice constants of the rhombic unit cell derived from the x-ray goniometric diagram by the present author are recorded: $a=12.60$ A.U., $b=8.20$ A.U., $c=8.91$ A.U. Naturally Morss was not able to decide which of his two lattices was correct, but it is now evident, as a result of the goniometric measurements of the present author, that cell II is actually the correct one.

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* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Zeitschrift für Physikalische Chemie*, Abt. B, Vol. 43, No. 4, pages 272-273, July 1939. This also constitutes the 15th communication of the author on x-ray studies.

LIGHT SCATTERING IN STRETCHED RUBBER *

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1

It is already known that when pure rubber is stretched in one direction it acquires a lustre¹. This means that light falling upon it is scattered with appreciably different intensities at various angles to the direction in which the rubber is stretched. In view of this and in connection with earlier experiments², a study of the scattering of visible light by stretched rubber was undertaken and the first results are reported in a brief way in the present paper.

First of all, however, it is well to describe the experimental apparatus and technique which were used.

A practically parallel, sharp beam of light was produced, the direction of which may be represented by the X-axis of a system of right-angle coördinates. The rubber test-specimen, in the form of a strip, was placed in such a position in the path of this beam of light that it was illuminated by the beam at right angles to its surface. In other words, the specimen lay in the YZ plane of the coördinate system and by means of a special device it could be stretched in the Z direction. At a suitable distance behind the test-specimen a smooth, transparent paper screen was placed, likewise at right angles to the direction of the beam of light. The distribution of the scattered light around the bright spot formed by the transmitted light could be observed by eye and could be photographed by a camera.

Samples of rubber as nearly pure as possible and containing no fillers were examined, including not only films prepared from pure unvulcanized and partially vulcanized latex, but also strips prepared from commercial sheets of "patent rubber" and from Para rubber.

2

As was to be expected, when an unstretched, and therefore isotropic, rubber film was illuminated in the way described, a strictly symmetrical, circular halo appeared on the paper screen, and its dimensions depended solely on the turbidity of the specimen. When the film was stretched to a higher degree, the halo became larger in the direction (Z) of stretching, at right angles to the plane XY, and finally at high degrees of elongation its form became that shown in the photograph reproduced in Figure 1. Scattered light could then be detected around the test-specimen in the plane (XY) perpendicular to the direction of stretching.

This phenomenon is essentially a surface effect, for in the case of test-specimens prepared from pure (i. e., unloaded) rubber, the light-scattering on the rough surfaces greatly exceeded the internal scattering. When stretched, the irregularities on the surface were extended in the direction of stretching to the same degree as was the whole test-specimen itself, so that the roughness became

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unidirectional and hence resembled a fibrous structure. Light falling on this striated surface was scattered by refraction, reflection and diffraction in a plane perpendicular to the direction of these fibres.

The lustre of stretched rubber, which is visible directly by eye, is therefore essentially the same as this surface phenomenon.

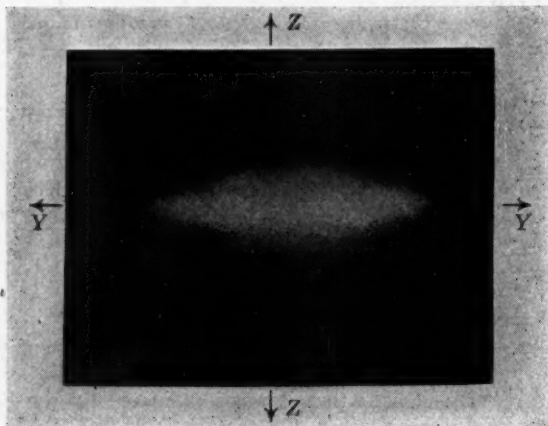


FIG. 1.

3

To study the scattering of light inside rubber, the surface effect was eliminated by immersion of the test-specimen in a liquid having the same index of refraction ($n=1.52-1.53$) as the rubber. In this way the amount of scattered light was of course greatly reduced, and the test-specimens became almost completely transparent. In the case of unstretched test-specimens, the scattered light which still remained was again visible in circular, symmetrical form. However, when the rubber was stretched, the form on the screen became of the type shown in Figure 2. This same form was observed when surface scattering was eliminated, not by immersion in a liquid, but by pressing test-specimens between two parallel, flat glass plates.

The figure representing the light scattering comprised, in the first place, a central band corresponding to a scattering of light in the plane (XY) perpendicular to the direction of stretching (Z), and in the second place two crossed bands to which corresponded a scattering of light in two planes cutting one another in the prolongation of the primary beam X. The angle α between these two crossed bands changed with increase in elongation of the rubber, *i. e.*, it decreased from large values at low elongations, *e. g.*, 60° at 120 per cent elongation, asymptotically to zero value. At the same time the bands became sharper. Furthermore in contrast to the effect described in Section 2, the bands appeared only at a definite minimum degree of elongation of 100 to 200 per cent.

With many samples the two crossed bands were slightly curved. This was especially evident with very thin films, so that it seemed as if they were formed from four branches of two curves of the character of hyperbolae. When test-specimens of rubber were irradiated with polarized light, it was found that the

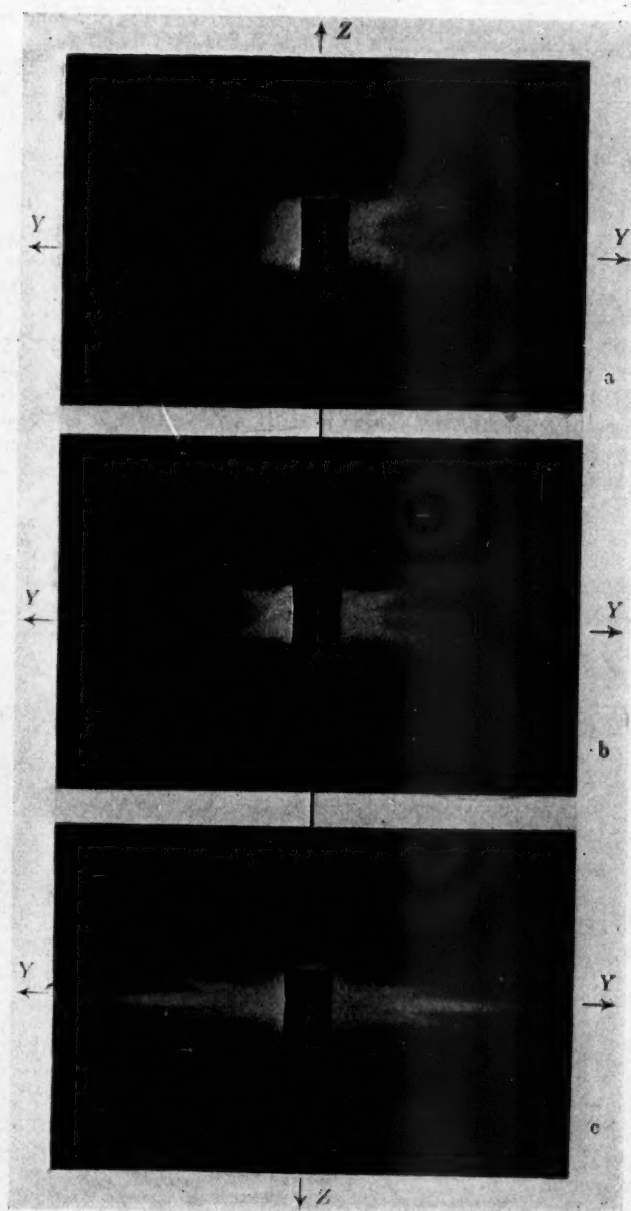


FIG. 2.

brightness of the scattered light depended to a great extent on the direction of vibration of the light, and the effect on the central band was different from that on the two outside bands. This indicated that the central band on the one hand and the two outside bands on the other hand were attributable to different scattering systems. Also in favor of this view is the fact that when rubber is illuminated with white light, the central band frequently has a somewhat different color tone from that of the outside bands. In general, however, the light scattering actually observed, except for the slight differences in color just mentioned, was independent of the wave length of the light, and hence it follows that light scattering is caused by structures whose dimensions exceed considerably the wave lengths of visible light.

The presence of three bands in the photographs of scattered light leads to the conclusion that three corresponding distinct directions must be present in stretched rubber and that these directions lie perpendicular to the directions of the bands³.

The direction of stretching, *i. e.*, the fibre structure, corresponds to the central band, and the two crossed, preferred directions perpendicular to the two crossed bands correspond to the latter. These directions are characterized by the fact that the refractive index in the longitudinal direction undergoes practically no important changes perpendicular to them.

4

In the light of these results, the rubber samples were examined in a polarizing microscope. Not only was the preferred direction which coincided with the

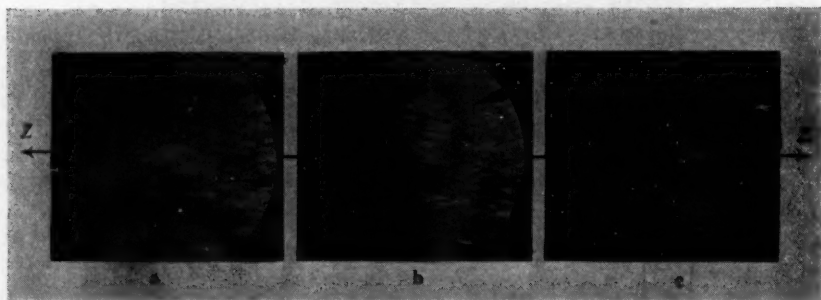


FIG. 3.

direction of stretching visible, even with moderate magnification but, by suitable adjustment of the polarizer and analyzer, two more crossed directions became visible. The effects seen under the microscope varied greatly, but in all cases they resembled a rhombic network or mosaic. Figure 3 shows three representative photomicrographs of these effects, corresponding to the three pictures of light scattering shown in Figure 2. Angle γ between the two directions of the network and angle α in the reproduction of scattered light differed only by a few degrees, and both angles showed the same changes with increase in elongation. This may be considered as proof of the causal relation between the observed network structure and light scattering. The order of magnitude of the rhombic structure was 0.01 to 0.1 mm., at least for the particular samples examined, the thickness of which was several tenths of a millimeter.

However, when examined under a magnification of 300 to 500, the relatively coarse structure of many of the rubber samples which has just been described was found to be made up of a much finer structure. It was necessary only to adjust the polarizer so that the electric vector was parallel to the direction of stretching; under these conditions there was visible, for all settings of the analyzer, a multitude of colorless, rod-shaped or threadlike structures, which were tightly interlaced, yet at the same time were all oriented in the two directions mentioned.

Naturally this microscopic examination furnished information only as to the relations existing in the plane observed under the microscope, *i. e.*, planes parallel to the flat surface of the rubber bands. Nevertheless, based on the principles of symmetry, one may assume that the same structural form is to be found in every other plane parallel to the direction of stretching (Z), provided that the specimen is sufficiently thick. The structure would necessarily have a statistical symmetry of rotation with respect to the direction of stretching. In support of this idea is the fact that the picture of the light scattering did not change perceptibly when the specimen of rubber was rotated around the direction of stretching (Z), *i. e.*, so that the light fell upon it obliquely. On the other hand, with very thin specimens of rubber, in which case the thickness was of the same order of magnitude as the dimensions of the elementary structure, a derangement of the statistical symmetry of rotation naturally was to be expected. Indications of this were obtained in these investigations of light scattering.

The lack of sharpness of the bands of scattered light corresponded to the irregularities in structural form which could be observed by microscopic examination. With the same specimens, the light-scattering effect and the structure, or more exactly angle α and angle γ , were reversible and reproducible by stretching, the only exceptions to this being cases where, with certain samples of rubber, hysteresis effects in both phenomena were observed. Finally it was discovered that, by warming the test-specimens, both the rhombic structure and at the same time the light-scattering effect could be made to disappear.

Where in the foregoing description the expression "structure" has been employed, this has been done with necessary reservations. To what extent the forms which were actually observed are to be regarded as the true structure, and whether they are of such a character as to complete present-day concepts of the structure of stretched rubber, remains to be seen.

ACKNOWLEDGMENT

The author wishes to show his sincere appreciation for the aid which he received from the Director of the Institute, Professor Edgar Meyer.

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APPLICATION OF THE INTERFEROMETER TO THE MEASUREMENT OF DIMEN- SIONAL CHANGES IN RUBBER *

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I. INTRODUCTION

The interferometer method for the measurement of small dimensional changes, previously used for many other materials, has been adapted in the present investigation to measurements on soft rubber. This method, which involves the counting of interference fringes of light of known wave length, was originated by Fizeau and developed by later workers. It has been most frequently applied to the measurement of thermal expansion. Merritt¹ has described the principles and the procedure which have been commonly followed at this Bureau in measurements of thermal expansion by the interference method. Measurements have been made on metals², glass³, and ceramic materials⁴, especially at elevated temperatures.

The interference method has not been hitherto applied, however, as far as we are aware, to measurements on any of the various forms of rubber, with the single exception of ebonite, or hard rubber⁵. The relatively easy deformation of most kinds of rubber gives rise to problems which do not occur in the application of the interferometer to most other materials. It is the purpose of this paper to discuss the apparatus used and the technique employed in the measurements of dimensional changes in rubber and to give consideration to the advantages and limitations of the method in its application to rubber. Particular emphasis is laid on measurements at temperatures as low as that of liquid air for the determination of expansivity and of the dimensional changes and temperatures involved in transitions between different forms of rubber. The method is not limited to measurements at different temperatures, however. It may be used in any case in which the measurement of dimensional changes is required. Possible applications of this sort are the measurement of the swelling of rubber by vapors and the determination of stress-strain relations under compressive loads.

II. PREPARATION OF SPECIMENS

The specimens, which were placed between the two interferometer plates, usually had a thickness of about 3 or 4 mm. Two different types were utilized, the first a set of three small separate blocks⁶ a few millimeters on an edge, and the second a ring about 21 mm. outside diameter and about 15 mm. inside diameter.

The small blocks were cut out by a device consisting of two single-edged safety-razor blades fastened on a steel bar, which was mounted by means of a hinge arrangement on a wooden base. The spacing of the razor blades, which were parallel and about 3.5 mm. apart, determined the thickness of the specimens and made these thicknesses very nearly the same. No particular effort was made to obtain uniformity in the other two dimensions. After a considerable number

* Reprinted from the *Journal of Research of the National Bureau of Standards*, Vol. 23, No. 5, pages 571-583, November 1939.

of specimens had been cut from the same sample, three of them were inserted between the interferometer plates, and substitutions of other specimens were made, if necessary, until there were not more than 10 interference fringes visible across the face of the plate. In this manner, three blocks were selected which were of the same height to within a few wavelengths of light.

The ring specimens were cut with a die in an arbor press in the manner commonly used in the preparation of specimens for tensile tests. In this case, the height of the specimen, of course, was not changed by the cutting. Even from ribbed smoked sheet, it was found possible by cutting a large number of rings to select satisfactory specimens.

III. APPARATUS

A diagram of the major part of the apparatus is shown in Figure 1. It is essentially the same as that designed by Souder and Peters⁷, with modifications

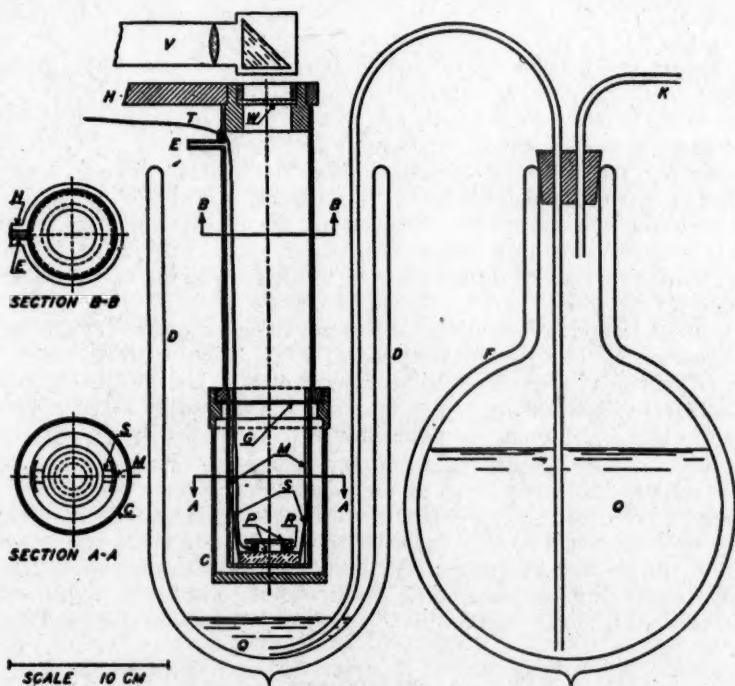


FIG 1.—Cross-section of the apparatus.

C, removable part of the container; *D*, Dewar flask; *E*, metal tube; *F*, spherical Dewar flask; *G*, leather gasket; *H*, arm supporting container; *K*, glass tube; *L*, glass tube; *M*, strips holding support for interferometer plates; *P*, interferometer plates; *Q*, liquid air; *R*, rubber specimen; *S*, flat steel springs holding lower interferometer plate in place; *T*, thermocouple leads; *V*, viewing instrument; *W*, window.

for work at low temperatures. The rubber specimen, *R*, separates two interferometer plates of clear, transparent fused quartz, the surfaces of each of which have been polished optically flat. The surfaces of the upper plate are inclined to each other at an angle of about 20 minutes to separate the reflections

of the images from the upper and lower surfaces. A finely ground surface on the bottom of the lower plate avoids undesirable reflection from this surface. The upper plate used in most of this work was 2.65 cm. (1.05 in.) in diameter, 0.635 cm. (0.250 in.) in thickness, and weighed 7.85 g. The lower plate is held in position on its support by two flat steel springs, *S*, one on each side. The springs are fastened to the two strips, *M*, which hold the support.

A bar, *H*, the height of which is adjustable by means of a rack and pinion not shown, supports the whole assembly. A removable part, *C*, of the container can be screwed to the stationary part, the joint being made tight by means of a leather gasket, *G*.

The temperature of the specimen is measured by means of a two-junction copper-constantan thermocouple placed between the interferometer plates and almost in contact with the specimen. The electromotive force of the thermocouple is read by means of a potentiometer. The leads, *T*, of the thermocouple pass through a small hole in the wall of the container near the top, the opening being sealed with wax. The reference junction is placed in a water bath in a small Dewar flask. The temperature of the bath is read on a mercury thermometer graduated to 0.1° C. and changes only very slowly.

For measurements below room temperature, cooling is effected by means of liquid air. A Dewar flask, *D*, is placed around the container, *C*. A glass tube, *L*, extends to the bottom of this Dewar and to the bottom of a spherical Dewar, *F*, the liquid-air reservoir. Pressures above or below atmospheric applied through glass tube *K* make it possible to raise or lower the liquid-air level in Dewar *D*, and thus to control the temperature of the specimen.

For measurements above room temperature, the Dewars are removed, and a vessel of water or some high-boiling oil is placed around container *C*. This can then be heated by an electric hot plate in which the current can be controlled by slide-wire resistors.

Experimental observations are made through the glass window, *W*, at the top of the container. The viewing instrument, *V*, is of the Pulfrich type⁸. The source of light is an electric discharge tube containing helium. When operated from a 10,000-volt transformer, this tube emits a spectrum, the effective component of which is the prominent yellow line with a wave length of 5876 Å.

The height of each specimen at room temperature can be measured by means of some suitable instrument, such as the double-contact screw micrometer gage of the type designed earlier by Holt⁹, who has since improved the design of the electric-contact indicator by the substitution of a small neon lamp operated from the 110-volt line. The height of the specimen is obtained in this manner as the difference of readings taken on the interferometer plates, first with the specimen in position for measurements and then with the plates in contact with each other.

IV. PROCEDURE

The specimens must be placed in the apparatus in such a way as to make visible a relatively small number of interference fringes and to eliminate errors caused by the tilting of specimens. The condensation of moisture on various parts of the apparatus necessitates certain precautions as the temperature of the specimens is varied.

1. PLACEMENT OF SPECIMENS

It was found desirable that both types of specimens, before being placed in the interferometer, have their upper and lower surfaces lubricated with finely

powdered graphite, such as Acheson No. 2301. After a liberal application of the graphite, the surface was rubbed on a sheet of paper to remove the excess of lubricant. Direct observation with the screw-micrometer gage showed that there was no appreciable change of the measured thickness occasioned by this operation. Lubrication of the surface was necessary, as is explained below, to avoid difficulties caused by dimensional changes in the rubber in directions parallel to the interferometer plates.

After three block specimens of nearly equal height had been selected and lubricated as described, they were placed between the interferometer plates, near the edge of the upper plate and equidistant from each other. Next it was necessary to determine which of the specimens had the greatest height. This could be accomplished by pushing down gently on the center of the top interferometer plate, and noting the direction of motion of the fringes, which is necessarily toward the point of greatest thickness.

The highest specimen was next moved toward the center of the plates, so that the load supported by that block could be increased from about one-third the weight of the upper plate to any desired value up to nearly the whole weight of the plate. The increased load on the highest block decreased the number of visible interference fringes, making the blocks, through the increased load, more nearly equal in height. Adjustment was made in this manner until not more than six or seven fringes appeared in the field of view.

It was next necessary to locate the point of contact carrying the greatest load. After a gentle tapping of the container supporting the plates, the interference fringe passing through the point of contact would remain stationary, while the other fringes would vibrate for a brief interval. The viewing instrument then was adjusted so that its cross hairs coincided with the point of contact.

A procedure essentially similar was followed when ring specimens were employed. Pressure applied on the top of the upper plate indicated which part of the specimen was highest. The ring was then moved so as to bring the high part closer to the center of the upper plate. The remainder of the procedure was the same as with the block specimens.

2. ELIMINATION OF ERRORS ARISING FROM TILTING

This method of making observations at the point of greatest load on the block specimens was suggested by J. B. Saunders, of this Bureau, who has recently discussed the matter with particular reference to glass specimens¹⁰. The method eliminated difficulties arising from the tilting of block specimens. Because of the difference in thermal expansivity between the specimens and the interferometer plates, there must be some relative motion of the surfaces of specimens and plates as the temperature is varied. If the surfaces are well lubricated, as by the use of graphite in the present work, this motion can take place as uniform slippage. If, however, there is sticking in at least two specimens at points which are not immediately above each other, tilting of the specimens must occur, with consequent changes in the distance between interferometer plates. Such changes, of course, lead to false values for the expansivity, since the effective height of the specimen varies with the angle of tilt. An analysis of the stability of the system shows that a decrease in the angle of tilt at the specimen which is most heavily loaded, with consequently increased angles of tilt at the other specimens, results in a lowering of the center of gravity of the upper plate. Therefore, in actual practice all the tilting will occur at the lightly loaded specimens, and

measurements at the point of contact of the most heavily loaded specimen will free the data from this error. Tilting of the lightly loaded specimens gives rise to a tilting of the upper interferometer plate. Such tilting, when it occurs, is evidenced by a change in the width of the interference fringes and consequently in the number of fringes visible. Thermal expansion alone causes a change in the width of the fringes of only the same percentage as the expansion itself. Since the expansion amounts to less than 3 per cent over the whole range of temperature studied in the present work, and since changes of this amount in the width of the bands are almost unobservable, appreciable changes in the number of visible interference fringes may be ascribed entirely to sticking of the surfaces with consequent tilting.

Sticking of the surfaces of the ring and interferometer plates gives rise to deformations producing changes in the effective height of the ring, in a manner similar to the tilting of the block specimens. In this case, however, false values of the expansivity cannot be avoided by taking observations at the point of heaviest loading. It is, therefore, essential with ring specimens to avoid all sticking by the liberal application of lubricant. In some cases tapping of the container was found necessary to bring about slippage.

3. ELIMINATION OF MOISTURE

Since the presence of moisture inside the apparatus gives rise to difficulties, the container should be closed tightly. The removable part, *C*, was consequently brought up around the specimens and screwed tightly in place. It was necessary, of course, during this process to avoid severe jolts, which might disturb the interference fringes. The joint was next wrapped with several turns of rubber tape, so that any water formed by condensation on the outside of the container might run down past the joint and not penetrate the leather gasket. The container was next evacuated through tube *E* and then filled with air which had been dried by passage over calcium chloride. If this were not done and if, consequently, water vapor in appreciable quantity were present inside the container, condensation would occur on the interferometer plates during warming from the lower temperatures, since the plates are then colder than the metal parts on which the vapor condenses during cooling. The presence of small amounts of condensed vapor on the plates can be tolerated, but beyond a certain limit light is no longer regularly reflected from the surfaces of the plates, and the field of view becomes dark.

If the humidity of the atmosphere was at all high, condensed moisture collected on the top surface of window *W*, when the container was kept at the lowest temperature. As a temporary expedient, the moisture was wiped off with a bit of absorbent cotton whenever present in sufficient quantities to interfere with vision; but it was found to be much more satisfactory to reduce the humidity of the room by an appropriate air-conditioning unit.

4. CONTROL OF TEMPERATURE

For measurements below room temperature, liquid air was used as the cooling medium. An atomizer bulb of rubber was placed on tube *K* and used to force the liquid air from the spherical Dewar, *F*, through tube *L* into Dewar *D*. By careful control of the level in *D*, the rate of cooling or warming of the specimen could be kept less than 1° C. per minute, a value which it was found desirable not to exceed. The fringes passing the cross-hairs were counted during both

cooling and warming. The temperature was observed at the passage of every fifth fringe and on some occasions more frequently. The time also was recorded so that the rate of cooling or heating could be known. The temperature of the specimen, when the liquid-air level was brought to within a few inches of the top of Dewar *D*, became very nearly that of the liquid air, values lower than -180°C . being always obtained after thermal equilibrium. After the minimum temperature had been attained, a considerable portion of the liquid air was removed from Dewar *D* by reducing the pressure in Dewar *F* by means of a pump connected to tube *K*. In this manner, the temperature of the specimen was allowed to rise at a controlled rate.

Before beginning observations at elevated temperatures, the bath of water or oil was cooled about 10 or 20 degrees below room temperature, and the current in the hot plate adjusted to a convenient value. It was found desirable to make as few changes in the heating current as possible, ranges of at least 20° or 30° being covered without change of the current. The rate of temperature rise decreased, of course, over each range. Preliminary runs were used to determine the value of the heating current for each range so that the initial rate of temperature rise should not exceed about 1°C . per minute and so that the final rate should not be unduly small.

V. CALCULATIONS

The essential data obtained during a run consist of the number of fringes which have passed the cross-hairs, the corresponding voltage of the thermocouple and the temperature of the fixed junction. From these one can calculate the change in length of the specimen and its temperature. Since the light traverses the space between interferometer plates twice, the vertical displacement of the upper plate when one fringe has passed the cross-hairs is equal to one-half the wavelength. The change in length of the specimen between room temperature and any other temperature is obtained, therefore, by multiplying the number of fringes which have passed the cross-hairs by one-half the wavelength. At room temperature the effective wave length of the light used is $0.5876\ \mu$. At other temperatures the wave length is different because of the variation of the refractive index of air with temperature. A table of corrections¹¹ to take account of this fact and the method of application are found in the paper by Merritt.¹²

The temperatures were read from a large calibration graph, which had been prepared from the standard tables for copper-constantan thermocouples given in the International Critical Tables¹³. The procedure described there was followed, a comparison between the thermocouple and a standard thermocouple being made at the temperature of liquid air.

A few selected lines of typical data and calculated results are shown in Table I to illustrate the method usually followed. Columns 1, 2, 6 and 7 contain the quantities directly observed. The fourth column, "Air correction", contains values taken from Merritt's tables, for the correction for the change of refractive index of air with temperature. The seventh column gives the temperature of the fixed junction as read on the mercury thermometer. The next column gives the corresponding electromotive force obtained from the calibration curve of the thermocouple. The sum of this value and the potentiometer reading yields the potentiometer reading which would have been obtained had the fixed junction been held at 0°C ., and this sum is shown in the ninth column.

TABLE I

TYPICAL DATA AND CALCULATIONS

Original height of specimen $l_{20} = 0.372$ cm.Wave length of helium line, $\lambda = 0.5876\mu$.

$$\text{Value of } \frac{\lambda}{2l_{20}} = 0.790\mu/\text{cm.}$$

Time	N fringe number *	0.790 N (μ/cm)	Air correction (μ/cm)	ΔL_1 expansion (μ/cm)	Potentiometer reading (μV)	Temperature of fixed junction ($^{\circ}\text{C}$)	Fixed junction electromotive force (μV)	Thermocouple corrected electromotive force (μV)	Temperature ($^{\circ}\text{C}$)
9:00	-35	-27.6	0.1	-27.5	-1,310	23.6	1,900	590	7.4
9:02	-40	-31.6	.1	-31.5	-1,460	23.6	1,900	440	5.6
11:41	-283	-223.5	5.8	-217.7	-12,620	24.5	1,980	-10,640	-180.2
11:48	-283.7	-224.0	5.9	-218.1	-12,640	24.6	1,990	-10,650	-180.5

* N is the number of fringes which have passed the reference point, the negative value indicating contraction of the specimen.

VI. DIMENSIONAL CHANGES IN STARK RUBBER

The results obtained in a study of frozen rubber illustrate the type of work which can be done by this method. The form of frozen rubber investigated had a melting point above room temperature and has been called stark rubber by Pickles¹⁴ and by Whitby¹⁵.

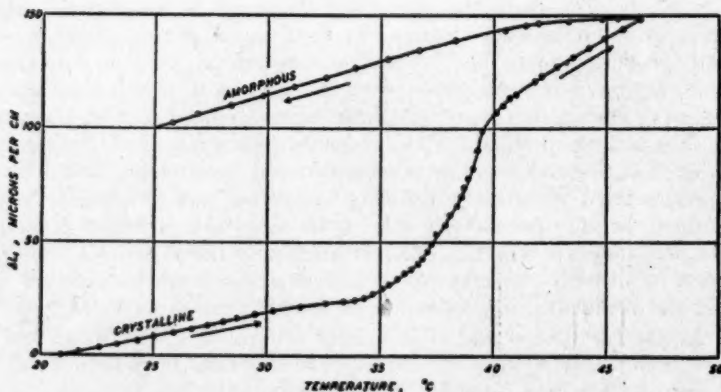


FIG. 2.—Dimensional changes during the melting of stark rubber.

The change in dimensions resulting from the melting of a specimen of stark rubber is shown in Figure 2. The sample, for which we are indebted to H. I. Cramer, of the University of Akron, had been in the frozen state for less than a year. The initial heating rate was approximately 0.4°C. per minute and decreased to about 0.16°C. per minute at the highest temperature. At this point the heating bath was removed and the specimen allowed to cool. The temperature decreased at an initial rate of about 0.95°C. per minute, and the rate diminished to less than 0.1°C. per minute at the last observation.

The difference in ordinates of the heating and cooling curves at 25°C. represents the difference in heights of the amorphous and the crystalline forms. It can be read from the graph as 91.5μ per cm. Assuming the specimen isotropic,

one finds that this corresponds to a volume increase of 2.77 per cent, a value not very different from those found¹⁶ at 0° C. for rubber which melted near 11° C. The general form of the graph is typical of the melting curve of rubber, but linear expansivities calculated from the slopes in Figure 2 are abnormally high, probably because the specimens were not lubricated during this particular run. The importance of lubrication was not appreciated at the time of this measurement.

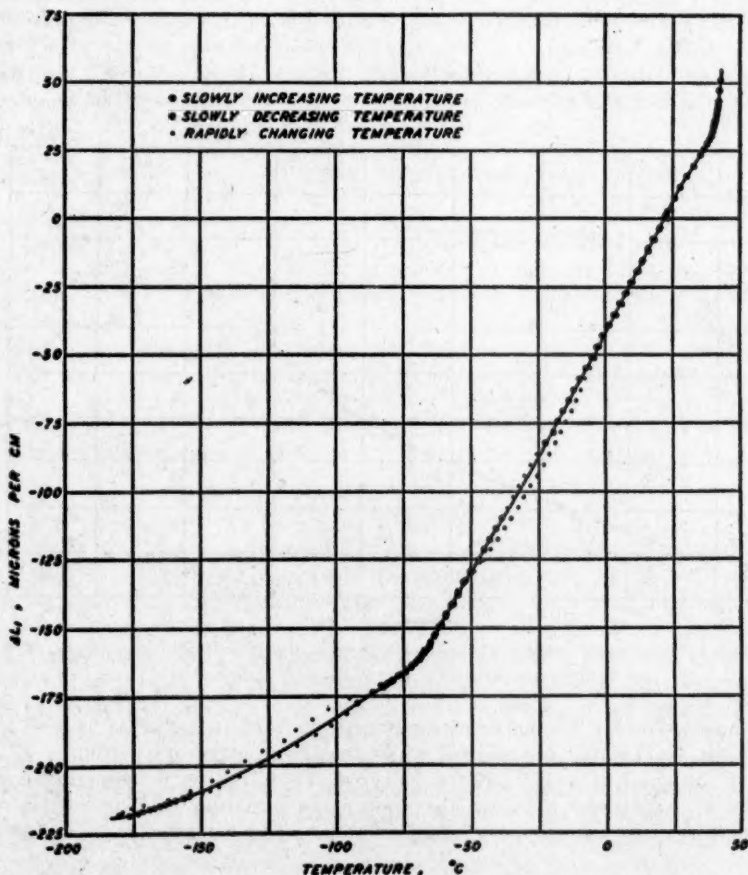


FIG. 3.—Dimensional changes in stark rubber.

The results of measurements of the dimensional changes in a different sample of stark rubber over a large range of temperatures are shown in Figure 3. We are indebted to G. S. Whitby for furnishing the sample, which had been in the frozen state for twenty-five years (from 1913 to 1938).

The specimens were cooled from room temperature to that of liquid air. They were allowed to warm up nearly to room temperature, and electric heating was then applied. The melting range in this case began at about 40° C., but observations could not be continued above 43° C., because at this point permanent deformation of the specimens under the weight of the upper plate occurred.

In Figure 3 the circles represent experimental points obtained when the temperature was changing at a rate of less than 1°C. per minute. Under these conditions it is thought that the difference between the actual effective temperature of the specimens and that indicated by the thermocouple is negligible. This is shown by the good agreement between the values obtained as the temperature was increasing (dark circles) and the values obtained as the temperature was decreasing (open circles). Observations made when the temperature was changing at a rate greater than 1°C. per minute are shown as dots. Under these conditions a difference between values obtained with increasing and decreasing temperatures can be seen.

The same data in the interesting region from -54° to -84°C. have been plotted on a much larger scale in Figure 4 to show the transition¹⁶ of the second

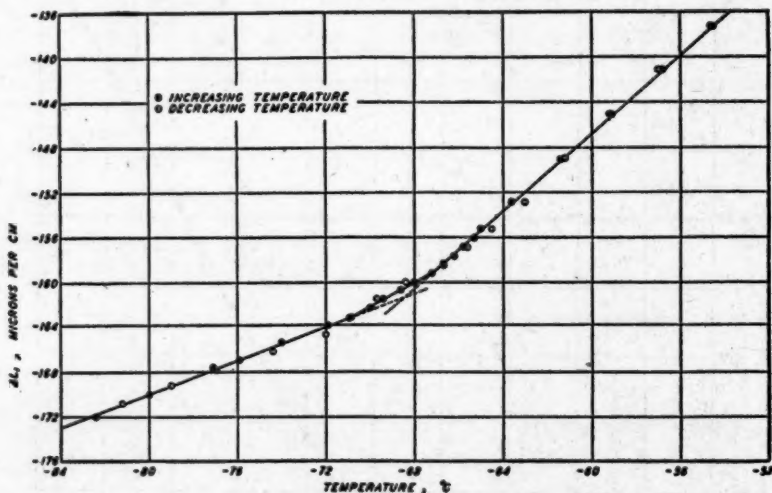


FIG. 4.—Dimensional changes in stark rubber passing through a second-order transition. This is a part of Figure 3 shown on a larger scale.

order near -70°C. The linear expansivity from -71° to -84°C. is read from the graph as 77×10^{-6} per degree, while the linear expansivity from -67° to -54°C. is found to be 175×10^{-6} per degree. These ranges of temperatures are, of course, insufficient to show the continuous variation of expansivity with temperature. The variation is evident over the larger ranges shown in Figure 3.

VII. ADVANTAGES AND LIMITATIONS OF THE METHOD

The interference method of measuring dimensional changes in rubber possesses certain advantages compared with other methods and, of course, certain attendant disadvantages. There are, in addition, certain limitations which restrict its use. The advantages and limitations will now be compared with those of the chief alternative methods.

1. DIMENSIONAL MEASUREMENTS

If there is reason to think that the rubber specimens are not isotropic, some method such as the interference method, by which one can measure separately

the three linear dimensional changes, is required. Any method involving merely the measurement of volume changes would give insufficiently detailed information about the changes in different directions.

2. SIZE AND SHAPE OF SPECIMENS

The interference method has been found more satisfactory for rubber than other familiar methods for linear measurements, which require a specimen in the form of a rod and which measure expansions by means of a dial gage^{16, 17}, optical lever or similar arrangement.

The interferometer specimens are very small and can easily be cut to shape. In spite of the small size of the specimens, the sensitivity of the method is quite great, since measurements of changes of length are made by comparison with the wave length of light. In the other methods, the specimens need to be much larger and must be formed or molded to a particular shape.

3. FORCE ON SPECIMENS

Most of the methods used for linear measurements exert some constraint on the rubber, either from the measuring mechanism or from the means of support. In the case of the interference method, the lateral constraint from the support is made quite small by the lubrication with graphite, but the vertical constraining force on the specimen due to the weight of the upper interferometer plate is, of course, of appreciable magnitude. This force is constant for a given plate and is of known size. Moreover, by the use of different plates, the force may be altered. Satisfactory plates weighing considerably less than 1 gram can be made.

4. PLASTIC FLOW

Plastic flow of the unvulcanized rubber was not observed at the lower temperatures and did not occur until temperatures somewhat above 40° C. were reached. The temperatures at which plastic flow began varied somewhat from sample to sample but could be located in each case within at least one half a degree. Plastic flow made interference measurements impossible on unvulcanized rubber at higher temperatures. With vulcanized rubber, no temperature limit set by plastic flow was observed in a series of measurements which extended to 100° C. No type of linear-expansion measurement can be free from the limitation caused by plastic flow, when it occurs. However small the constraining forces, this effect will occur at the higher temperatures, even under the weight of the specimen itself.

If the rubber is isotropic, methods which measure volume change can be utilized, and are necessary in cases where there is a possibility of plastic flow. A dilatometer with confining liquid has been used¹⁶ to measure volume changes in rubber, and is probably the most important alternative to the interference method. Here plastic flow is greatly reduced and, even when it occurs, does not alter the volume. The method can thus be used for unvulcanized rubber at higher temperatures.

5. CONFINING LIQUIDS

The interference method requires no confining liquid in contact with the rubber and is free from difficulties arising from the presence of the confining liquid usually necessary in a volume dilatometer.

None of the common liquids which are thought to be without swelling action on rubber remain liquid much below -100° C., and, in actual practice, work

using a confining liquid has been limited to the range above -85°C . because of the excessive viscosity of those liquids which do not actually crystallize above -100°C . The interference method is free from this temperature limitation, and measurements have been continued to temperatures as low as that of liquid air. With certain modifications of technique, the temperatures might be carried still lower to limits set only by the refrigerating liquid.

Furthermore, it has not been established that the presence of a confining liquid, even one which does not swell rubber appreciably, is completely without influence on the occurrence of transitions. For example, there seems to be evidence¹⁶ that the presence of acetone inhibits the second-order transition normally occurring near -70°C ., or at least lowers the temperature at which it occurs.

Other disadvantages of a confining liquid are the constant possibility of evaporation during a run, and the difficulties caused by the liberation of dissolved gases, as the temperature is raised. Usually, if a fair degree of sensitivity is required, ranges of not more than 30° or 40°C . can be covered without the addition or removal of liquid.

6. TEMPERATURE EQUILIBRIUM

In comparison with other methods for either linear measurements or volume measurements, the specimens used in the interferometer are quite small. Therefore, in addition to the resultant economy of material, there is the advantage that the attainment of temperature equilibrium throughout the rubber is relatively rapid. Consequently, changes of temperature can safely be made much more rapidly than in cases where large specimens are used, when the attainment of equilibrium is delayed by the relatively poor thermal conductivity of rubber. The expansivity over the range of temperatures from that of liquid air to room temperature can therefore be measured by the interference method in a single working day. With some of the other methods, observations must extend over several days. For dimensional changes of such nature as to require more than one day for completion, such as might occur during swelling and freezing, the interference method is not so convenient, since it requires continuous observation.

This inconvenience might be removed by adopting photographic recording¹⁸ or a different interference method involving the use of a block of fixed height and the counting of the number of interference fringes between two marks rather than the counting of the number of fringes which pass a given mark.

Because of the relatively rapid attainment of temperature equilibrium in the interference method, it is convenient to carry out measurements with decreasing temperatures as well as with increasing temperatures. Thus, any permanent distortion is immediately obvious.

7. CALCULATIONS

The calculation of expansivities from interference measurements is considerably simpler than from volume measurements. In the latter case, for example, it is necessary to take account of the expansion of the glass bulb and of the confining liquid, as well as to make corrections for the temperature of the exposed stem. The different amounts of confining liquid necessary for different temperatures ranges further complicate the calculations.

The interference method introduces no discontinuous intervals of temperature into the calculations. As shown by Figures 2 and 4, it can give results of considerable detail in studies of the nature of a transition.

SUMMARY

The interferometer method for the measurement of small dimensional changes is adapted here to measurements on soft rubber. A detailed description is given concerning the preparation of specimens, the apparatus, the procedure and the calculations necessary for the application of this method. Particular emphasis is placed on the measurement of thermal expansivity and the dimensional changes involved in transitions between the different forms of rubber. The lower limit of temperature is set only by the refrigerating liquid, temperatures as low as -185°C . being utilized. The upper limit of temperature is set only by the rubber itself. Results obtained in a study of the expansivity and transitions of "stark" (frozen) rubber are given as an illustration of the application of the method. Other possible applications are the measurement of the swelling of rubber by vapors and the determination of stress-strain relations under compressive loads. The chief limitation of the application of this method to rubber arises from the plastic flow of unvulcanized rubber at elevated temperatures. The method also possesses the inconvenience of requiring continuous observation. Compared with alternative methods of measuring small dimensional changes, the method possesses advantages arising from its high sensitivity, from the small size of the specimens required, from the ease of obtaining temperature equilibrium, from the absence of a confining liquid and from the simplicity of the calculations.

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STEROLS

L. THE ISOLATION OF CAOUTCHICOL *

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Led by the possibility of a new and better source of sterols, we recently have investigated the non-saponifiable fraction of an acetone extract of crude rubber known as jelutong.†

Whereas the sterol fraction of this substance was found to be quite small, a large quantity of a new substance of triterpenoid character was found to be present, and it is the isolation of this substance, which we have named *caoutchicol*, that is described in this paper. Preliminary attempts to crystallize the crude jelutong extract showed that it still contained some waxy ester-like substances; so the extract was rehydrolyzed with hot alcoholic potassium hydroxide. The non-saponifiable fraction after this hydrolysis was treated with digitonin to precipitate the sterols, but the quantity of precipitate which was thus formed was too small to permit a characterization of the sterols which it contained. The main component, which did not precipitate digitonin, was found to be an alcohol, *caoutchicol*, which was purified most easily by the preparation and crystallization of its high melting acetate. Hydrolysis of this acetate gave the original *caoutchicol*, for which analysis and molecular weight indicate the formula $C_{30}H_{50}O$. This compound possesses one active double bond, as shown by the formation of a crystalline dibromide from both *caoutchicol* and its acetate, and also the formation of a dihydro derivative by catalytic reduction in acetic acid, using Adams catalyst. This dihydro compound is saturated to bromine. A further proof that the substance contains only one hydroxyl group is the preparation of a ketone, *dihydro-caoutchicone*, by oxidation of the dihydro compound with chromic acid. This ketone was characterized by the formation of a *semicarbazone*. The fact that *caoutchicol* possesses thirty carbon atoms and does not precipitate digitonin suggests that it is closely related to the triterpenoids, and is probably not a sterol. Thus, it may be related to lanosterol and agnosterol.

We wish to thank Oliver Kamm and Parke, Davis and Company for their generous help and assistance in various phases of this work.

EXPERIMENTAL PART

CAOUTCHICOL.—The non-saponifiable fraction of an acetone extract of crude rubber known as jelutong was supplied to us by the B. F. Goodrich Company of Akron, Ohio. This product (35 g.) was resaponified by refluxing for one hour with alcoholic potassium hydroxide solution. Water was added and the product was filtered. It was dried by distilling benzene from it. The product was dissolved in 250 cc. of ethyl alcohol, and to this was added 5 g. of digitonin dissolved in 250 cc. of hot ethyl alcohol. After standing overnight the digitonide was filtered and dried (wt. 5.4 g.). After decomposition with pyridine, it gave a mixture of sterols which could not be separated because of the small quantity available.

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† Kindly supplied by B. F. Goodrich Company, Akron, Ohio.

The alcohol was removed from the filtrate of the digitonide and the residue was extracted with ether and filtered from unchanged digitonin. It was dried by distilling benzene from it, then converted into its acetate by refluxing with 100 cc. of acetic anhydride for thirty minutes. The product was collected at 0° and recrystallized from acetone and methanol. It is very insoluble in methanol and fairly soluble in acetone, crystallizing in needles melting at 216°.

Anal.—Calcd. for $C_{32}H_{52}O_2$: C, 81.9; H, 11.2; mol. wt., 468. Found: C, 81.8; H, 11.2; mol. wt. (Rast), 472.

To a solution of 100 mg. of the acetate of *caoutchicol* in 5 cc. of ether was added a slight excess of molar bromine solution in acetic acid. The ether was evaporated and the residue was crystallized from acetone. It melted at 225° with decomposition.

Anal.—Calcd. for $C_{32}H_{52}O_2Br_2$: C, 61.1; H, 8.4. Found: C, 61.1, H, 8.3.

A solution of 100 mg. of the acetate of *caoutchicol* in alcohol was hydrolyzed by refluxing with alcoholic potassium hydroxide for thirty minutes. After crystallization from methanol and acetone, it melted with decomposition at 205–210°, and gave no precipitate with alcoholic digitonin.

Anal.—Calcd. for $C_{30}H_{50}O$: C, 84.4; H, 11.8. Found: C, 84.6; H, 11.8.

To a solution of 100 mg. of *caoutchicol* dissolved in 5 cc. of ether was added a slight excess of a molar bromine solution in acetic acid. The ether was evaporated and the residue crystallized from acetone. It melted at 186–190° with decomposition.

Anal.—Calcd. for $C_{30}H_{50}OBr_2$: C, 61.4; H, 8.6. Found: C, 60.9; H, 8.4.

DIHYDROCAOUTCHICOL ACETATE.—A solution of 1 g. of *caoutchicol* acetate in 100 cc. of acetic acid was shaken with 500 mg. of platinum oxide under a pressure of 45 pounds (3 atm.) of hydrogen at 70° for three hours. The catalyst was filtered, the solvent removed, and the residue crystallized from acetone, methanol and acetic acid. It melted at 247°.

Anal.—Calcd. for $C_{32}H_{54}O_2$: C, 81.6; H, 11.6. Found: C, 81.6; H, 11.4.

DIHYDROCAOUTCHICOL.—A solution of 500 mg. of *dihydrocaoutchicol acetate* in alcohol was refluxed with an excess of alcoholic potassium hydroxide for thirty minutes. After crystallization from acetone and methanol, the product had a melting point of 188°.

Anal.—Calcd. for $C_{30}H_{52}O$: C, 84.0; H, 12.2. Found: C, 83.8; H, 12.1.

DIHYDROCAOUTCHICONE.—To a solution of 200 mg. of *dihydrocaoutchicol* in 20 cc. of acetic acid was added 60 mg. of chromic oxide in 3 cc. of 90% acetic acid. After standing at room temperature for one hour the crystalline product which separated was filtered and recrystallized from acetone to a constant melting point of 210°.

Anal.—Calcd. for $C_{30}H_{50}O$: C, 84.4; H, 11.8. Found: C, 84.2; H, 11.8.

A solution of 20 mg. of *dihydrocaoutchicone* in alcohol was heated on a steam-bath with 20 mg. of semicarbazide hydrochloride and 20 mg. of sodium acetate for one hour. It was poured into water, filtered and recrystallized from acetone to give the *semicarbazone*, m. p. 249–250°, dec.

Anal.—Calcd. for $C_{31}H_{53}N_3O$: C, 77.0; H, 11.0. Found: C, 76.9; H, 11.0.

SUMMARY

Caoutchicol ($C_{30}H_{50}O$), a new alcohol, was isolated from a crude rubber extract (jelutong). It does not precipitate digitonin. It forms a *monoacetate*, a *dibromide* and can be reduced to a *dihydro derivative*. *Dihydrocaoutchicol* forms the ketone, *dihydrocaoutchicone*, on oxidation.

DYNAMIC FATIGUE LIFE OF RUBBER *

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If a rubber member is continuously vibrated it will sooner or later crack and ultimately rupture, owing to the repeated oscillations to which it has been subjected. The gradual deterioration of physical and chemical properties which accompanies such vibration is called dynamic fatigue. The number of such repeated vibrations required to rupture the rubber member is here defined as the dynamic fatigue life of the member for the particular condition of vibration imposed. The authors wish to outline briefly the general nature of the results they have obtained in their studies on the dynamic fatigue life of rubber and,

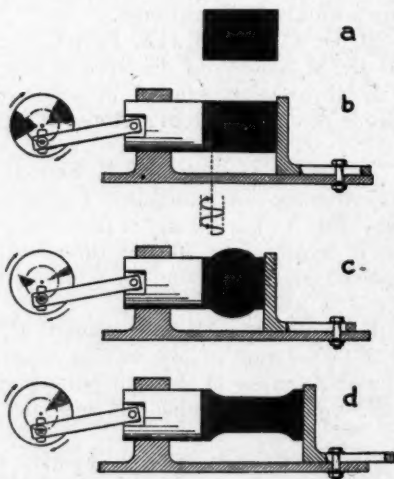


FIG. 1.—Rubber sample in idealized test machine.

in particular, to show the critical dependence of the life on the imposed oscillation conditions.

The dynamic fatigue life of rubber which is being vibrated linearly, that is, back and forth along its own length, between constant strain limits will be discussed first. Figures 1 to 3 facilitate a general statement of the problem and also serve to define certain oscillation limits which are of fundamental importance with reference to dynamic fatigue life. The sketches are conventionalized for the sake of simplicity.

In Figure 1, *a* is a side view of a cylindrical body of rubber bonded between two circular metal end plates. In *b* this rubber member has been placed between two heads of a test machine; the position of the stationary head is adjustable; the other head oscillates back and forth in a direction parallel to the axis of the rubber sample. *b*, *c*, and *d* show various possible test conditions resulting from variation

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of the position of the adjustable head. Besides the alteration of the adjustable head (which does not change the oscillation stroke) the stroke itself can be changed by varying the position of the eccentric connection on the rotating wheel.

In Figure 2, *a* again represents the rubber sample. Its free unstrained length is referred to as L_0 . *b* and *c* show the two extremes in length assumed by the rubber member for a particular oscillation condition. The minimum length, which is the condition in *b*, is referred to as L_{min} . The maximum length of the sample in the oscillation, as illustrated in *c*, is referred to as L_{max} . The difference between L_{max} and L_{min} is the oscillation stroke, ΔL . The actual fatigue machines used in the authors' experimental testing are designed so that ΔL and L_{min} can be varied independently.

In the following discussion "per cent oscillation stroke" and "per cent minimum strain" are mentioned. To comprehend the significance of the fatigue data it

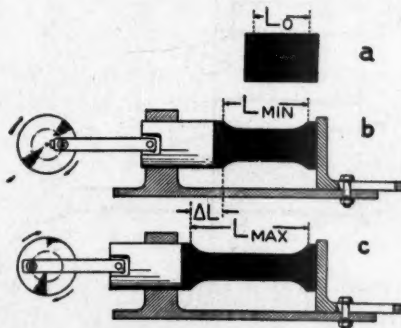


FIG. 2.—Rubber sample in idealized test machine.

$$\frac{\Delta L}{L_0}(100) = \% \text{ oscillation stroke}$$

$$\frac{L_{min} - L_0}{L_0}(100) = \% \text{ minimum strain } \begin{cases} + \text{extension} \\ - \text{compression} \end{cases}$$

is necessary that these variables be clearly understood, for in the final analysis they do determine the fatigue life of a sample.

$$\% \text{ minimum strain} = \frac{L_{min} - L_0}{L_0} \times 100$$

$$\% \text{ oscillation stroke} = \frac{L_{max} - L_{min}}{L_0} \times 100 = \frac{\Delta L}{L_0} \times 100$$

These definitions involve three specific lengths of the sample (L_0 , L_{max} , and L_{min}) and are merely certain deformations expressed as percentages of the free unstrained length of the rubber.

Four different types of oscillation conditions for a constant oscillation stroke, ΔL , are illustrated in Figure 3. (*a* shows a compression vibration cycle in which the maximum length in the imposed vibration is less than the free unstrained length of the sample. *b* shows a compression-extension vibration cycle in which L_{min} is less than L_0 and L_{max} is greater than L_0 . *c* shows an oscillation condition in which L_{min} is equal to L_0 and L_{max} is greater than L_0 . *d* shows an extension oscillation cycle in which both L_{min} and L_{max} are greater than L_0).

The two fundamental problems that have been investigated quantitatively are: (1) If ΔL is kept constant, how does the fatigue life of a rubber unit depend on L_{\min} , for any value of L_{\min} ranging from high compression to any possible extension? (2) If L_{\min} is kept constant, how does the dynamic fatigue life of a rubber unit depend on the magnitude of ΔL ?

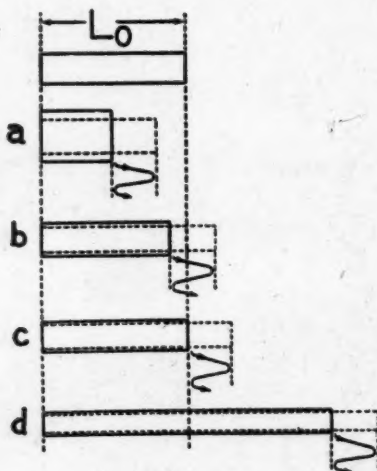


FIG. 3.—Types of oscillation conditions for constant oscillation stroke ΔL .

LINEAR DYNAMIC FATIGUE TEST SAMPLES

Figure 4 is a photograph of different types of rubber samples used by the authors in dynamic fatigue studies of rubber. They are cylindrical dumbbells of rubber bonded to metal bolt ends, shown at A and B. The effective rubber lengths varied from 2 inches (sample 1) to 0.125 inch (sample 13), and the ratios of diameter to length varied from 1/16 to 8.

MACHINES FOR TESTING DYNAMIC FATIGUE LIFE OF RUBBER

Figure 5 (upper) shows rubber samples, R , mounted in a slow-speed fatigue machine designed by the United States Rubber Company. The bottom bars, B , are held fixed and the top bars, T , are vibrated up and down. The rubber samples fastened between the two bars are vibrated through constant oscillation strokes which can have any value up to 3.5 inches. The minimum length of the sample in the vibration cycle can be varied either by adjustment of the separation between the bars or by variation of the point at which the bolt ends are attached to the bars. Both methods are clearly visible in the figure. The vibration frequency is 180 cycles per minute.

Figure 5 (lower) shows rubber samples, R , mounted in a high-speed dynamic fatigue machine, also designed by the United States Rubber Company. The two outer circular heads, O , are held fixed and the two inner circular heads, I , so-called "wobble plates", are mounted on a shaft arranged to give a nutational motion to the heads, which in turn vibrate all the rubber samples back and forth

along their own lengths. The minimum length of the sample in its vibration cycle can be varied by alteration of the separation of the plates, by the screw adjustment shown, or by variation of the point at which the bolt ends are attached to the plates. The machine is adjusted for a 0.5-inch stroke and vibrates at 3600 cycles per minute.

Figure 6 shows a DeMattia fatigue machine with rubber samples, *R*, being vibrated between a stationary head, *S*, and an eccentric driven head, *C*; this fatigue machine has a frequency of vibration of 660 cycles per minute; its stroke

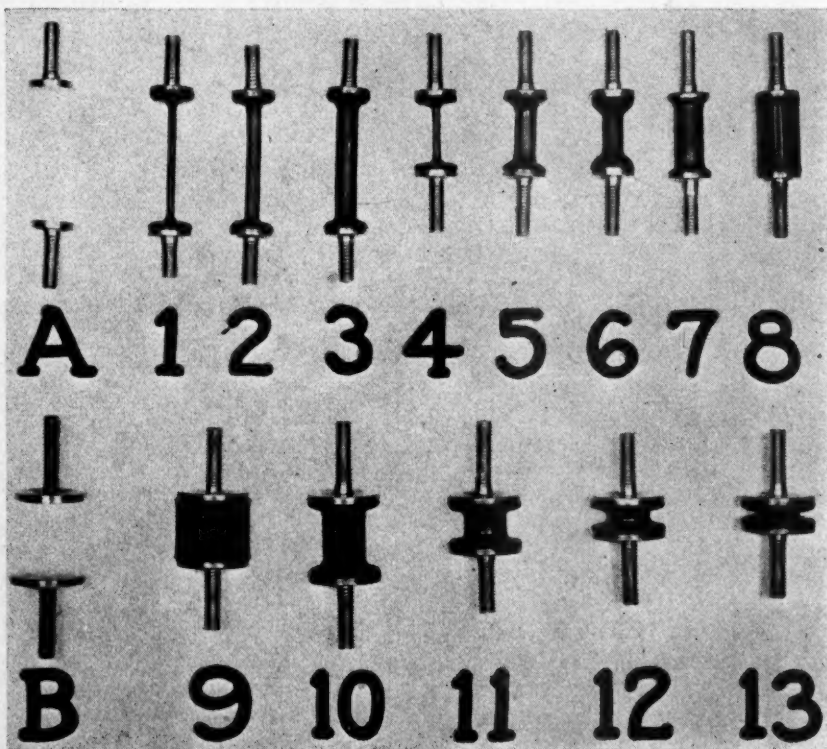


FIG. 4.—Types of rubber samples used in linear dynamic fatigue tests.

can have any value up to 2 inches. The fatigue machine on the right is another high-speed dynamic fatigue machine similar to the high-speed machine shown in Figure 5 (lower) but with a 0.25-inch stroke.

GENERAL NATURE OF LINEAR DYNAMIC FATIGUE LIFE CURVE

The general nature of the dynamic fatigue life curve for small oscillation strokes, say, of the order of 25 per cent, is illustrated in Figure 7. The per cent linear strain at the minimum length in the oscillation is plotted as abscissa. The number of cycles of vibration necessary to completely rupture the rubber, that is, its dynamic fatigue life, is plotted in arbitrary units as ordinate. The important feature of the dynamic fatigue life curve is that the rubber under linear

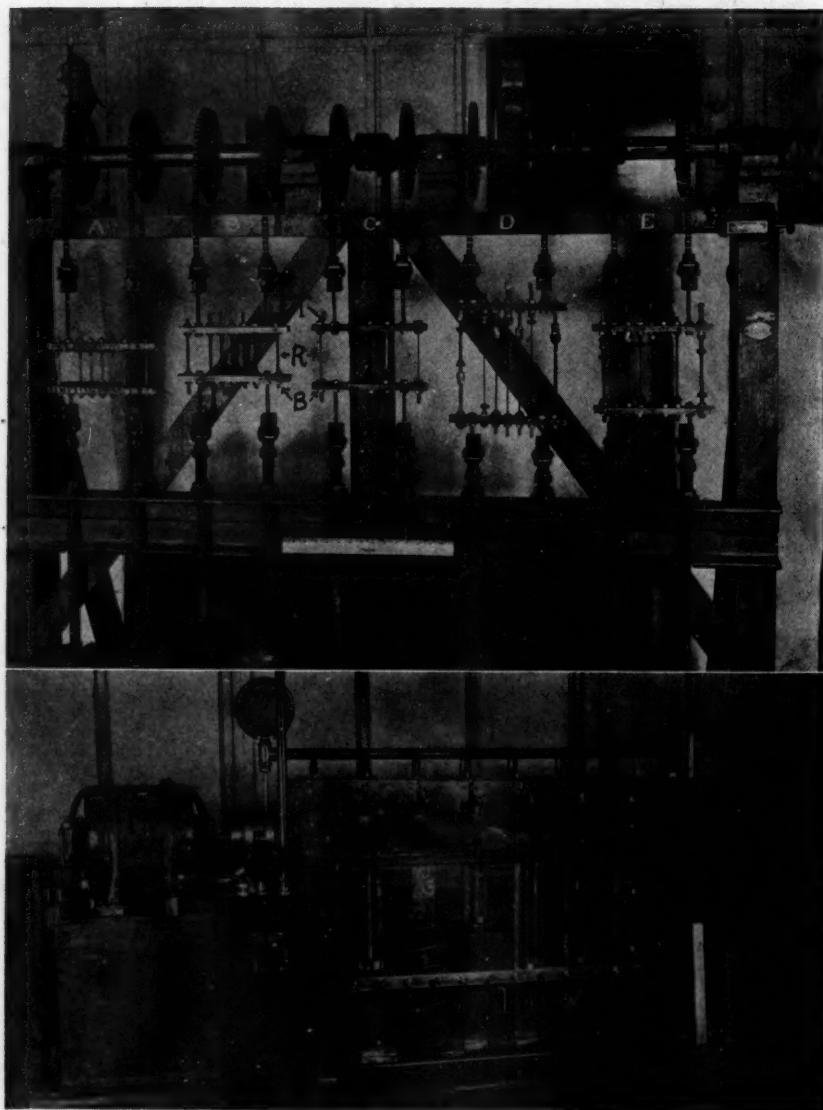


FIG. 5.

(Upper) Rubber samples mounted in slow-speed fatigue machine.
(Lower) Rubber samples mounted in high-speed constant-load fatigue machine.

vibrations exhibits a minimum dynamic fatigue life in the region where $L_{\min} = L_0$, that is, where the return stroke brings the sample back to a condition of zero strain. This minimum life is bounded both in compression and extension by regions of greater fatigue life. The general nature of the curve, a minimum bounded on two sides by maxima, remains the same whether the dynamic fatigue life is plotted as the number of cycles to break the rubber completely into two parts or is plotted as the number of cycles to produce a visible crack in the rubber.

Mention has been made in published articles^{1, 2, 3, 4, 5} that the mechanical fatigue resistance of rubber is less in extension when the minimum of the oscilla-

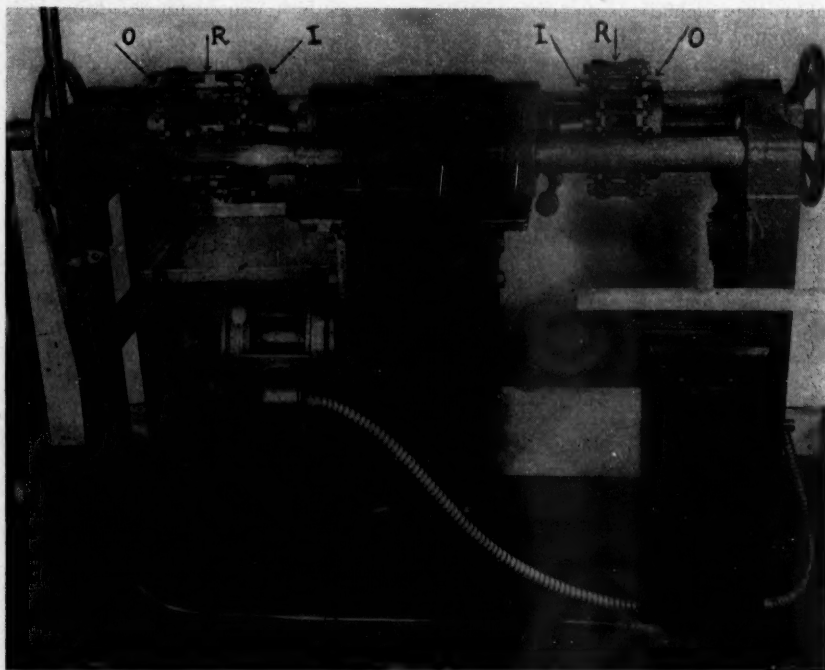


FIG. 5 (cont'd).

Rubber samples mounted in high-speed dynamic fatigue machine.

tion falls near zero strain. However, no complete study, as given in the present paper, has been published in which the fatigue lives of rubber have been investigated throughout the compression-extension region as a function of the strain or stress limits.

LINEAR DYNAMIC FATIGUE LIFE CURVES FOR A 50 DUROMETER STOCK

Figure 8 is a plot of experimental results obtained on a rubber stock which has a reading of 50 on a type-A Shore durometer. The data are for rubber worked indoors in artificial lighting and in the absence of oil, grease or other deteriorating chemical agents. The per cent linear strain at minimum length in the oscillation is plotted as abscissa. The dynamic fatigue life in terms of the number of cycles

for complete rupture is plotted as ordinate on a logarithmic scale. On a linear scale the difference in height between each maximum and its corresponding minimum would be greatly enhanced. For the 25 per cent oscillation, for example, the fatigue life at the minimum is about 6,000,000 cycles, while at the maximum in the extension region it is over 600,000,000 cycles or more than 100 times as great. The graph shows results for a series of different constant oscillation strokes varying from 25 to 350 per cent. Each experimental point represents numerical averages of from 1 to 20 sample breaks. The graph itself contains results on 450 samples of the 50 Shore durometer stock.

For small oscillation strokes, such as 25 or 50 per cent, there are two maximum fatigue regions, one in extension and the other in compression.

For large oscillations, for example, 300 per cent, there is no definite compression maximum.

For a given minimum strain length, the larger the oscillation stroke, ΔL , the lower the dynamic fatigue life of the rubber.

The fatigue life hump in the extension region shifts towards the origin as the oscillation stroke is increased.

This last point is partly due to choice of variables, since for a given stock the per cent elongation at break is a fairly definite quantity and as the oscillation stroke increases the L_{min} for which there will be a break in the first cycle decreases. No corrections have been made in this graph for rubber temperature variations resulting from fatiguing at different frequencies or from fatiguing samples of different sizes or shapes. However, when such corrections are made to, say, a rubber temperature of 100° F., the general nature of the curves remains the same.

All rubber stocks considered (which include stocks of hardnesses varying from 30 to 80 Shore durometer, type A) have similar fatigue life curves for constant strain conditions of oscillation. In general, for the same strain conditions of oscillation a harder rubber stock will have a lower fatigue life than a softer stock.

The compound formula for the 50 durometer stock whose experimental dynamic fatigue life curves are given in Figure 8 is the following:

Rubber	100
Carbon black	39
Zinc oxide	5.5
Stearic acid	1.5
Pine tar	4
Antioxidant	0.6
Retarder	0.2
Accelerator	0.8
Sulfur	2.9

EFFECT OF TEMPERATURE ON DYNAMIC FATIGUE LIFE

Figure 9 shows how the temperature of the rubber during oscillation affects its fatigue life. The graph is a composite one plotted to cover most of the rubber stocks with which the authors worked. The ratio of fatigue life at a given temperature to that at 100° F. is plotted as ordinate along a logarithmic scale. The temperature of the rubber is plotted as abscissa. The ordinate of the graph, in other words, gives the factor by which the fatigue life of rubber vibrating at a rubber temperature of 100° F. must be multiplied in order to give the fatigue life which would result for rubber vibrating under the same oscillation conditions but at the rubber temperatures given along the abscissa.

The temperature of the rubber under the imposed vibration has a pronounced effect on its fatigue life. Consider a sample vibrating under certain oscillation conditions and at a rubber temperature of 100° F. It will have a given fatigue life corresponding to the ratio =1. If an identical sample is vibrating under the same oscillation conditions but at a much higher rubber temperature, its fatigue life will be less because its deterioration results from several causes. There is first the effect which would result from merely the vibration at 100° F. Then there is the deterioration due to heat aging which would result from keeping the sample at this high temperature without vibration. The total deterioration in all probability is not the sum of these two parts. For example, there may be an interaction between temperature and oscillation which alters the amount of deterioration. Since the relative importance of these variables as well as their

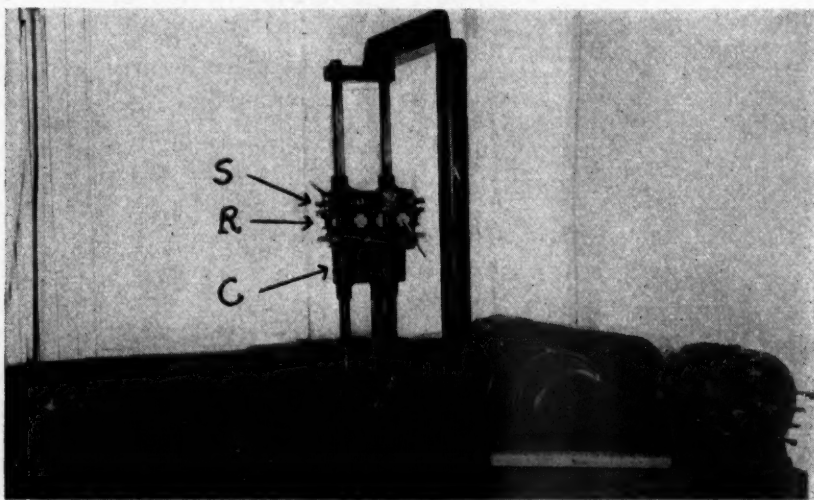


FIG. 6.

(Left) DeMattia fatigue machine with rubber samples.
(Right) High-speed dynamic fatigue machine, 0.25-inch stroke.

interaction cannot be given an evaluation applicable to all cases of rubber testing and compounding, the ratio for high temperatures is indicated as a broad band in Figure 9. Likewise, in the low-temperature region a broad band is also plotted. At the low temperatures the fatigue life depends, among other things, on the chill characteristics of the rubber stock and the total time during which the rubber member is being fatigued at the low temperature.

LINEAR DYNAMIC FATIGUE LIFE UNDER CONSTANT LOAD CONDITIONS

Figure 5 (center) shows a high-speed constant-load fatigue machine which vibrates the rubber samples at 1800 cycles per minute. The oscillation stroke on this machine can be varied from 0.125 to 0.75 inch. In this type of testing the rubber samples, *R*, are loaded with dead weights, *W*. The top of the rubber sample is vibrated up and down, the weights remaining stationary, owing to the mismatching of frequencies, that is, the frequency of the imposed vibration is

very much greater than the natural mechanical frequencies of the weights sprung on the rubber samples.

The distinction between this type of fatigue testing and the constant-strain fatigue testing is that in this case the rubber samples are allowed to drift, or extend in length with time, as they are being dynamically fatigued. However, the general nature of the fatigue life curves obtained under dead loading is similar to the fatigue life curves for constant strain oscillation; and the dynamic fatigue life under "constant load" fatigue conditions can be calculated from data obtained on constant-strain fatigue if changes in length accompanying dynamic drift are taken into account.

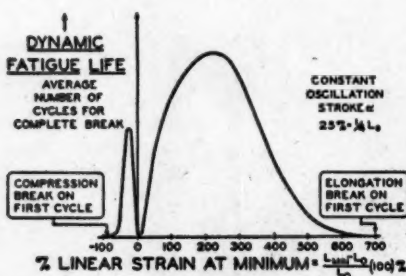


Fig. 7.—Dynamic fatigue life curve for small oscillation strokes.

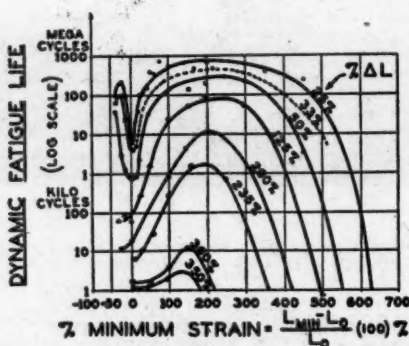


Fig. 8.—Experimental data on 50 durometer stock.

DYNAMIC FATIGUE LIFE OF RUBBER VIBRATED IN SHEAR

Until now we have considered only the dynamic fatigue of rubber worked under linear strains. Similar dynamic fatigue relations have been found for rubber vibrated in shear.

a in Figure 10 is a sketch of a double-shear unit which consists of two identical rectangular bodies of rubber of thickness T bonded between two outer metal plates and a central metal plate. If the central plate is displaced a distance d relative to the two outer plates the rubber is put in shear; and we express the magnitude of the shear deflection either as the shear ratio d/T or as the shear percentage $(d/T) 100$. *b* represents the two oscillation extremes of such a unit vibrated in shear. The minimum deflection in the shear cycle is d_{\min} ; the maxi-

mum, d_{\max} . The shear cycle is then specified as one of vibration between the shear percentages (d_{\min}/T) 100 and (d_{\max}/T) 100.

Figure 11 illustrates results obtained on shear samples of the 50 durometer stock discussed above. The two outer metal plates were held fixed, and the central plate was vibrated back and forth along its length between two extremes as shown by the dotted contours. The oscillation length was a 50 per cent shear oscillation. In shear mountings the rubber may be placed in lateral strains which are normal to the center plate. Three conditions of lateral strain are shown in

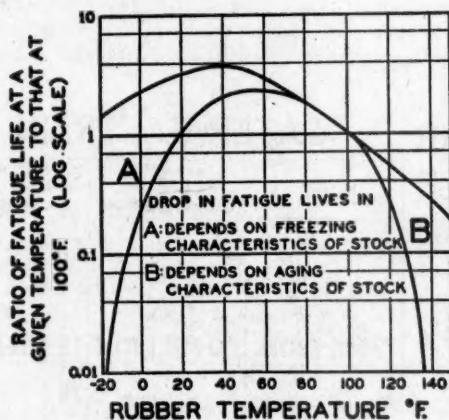


FIG. 9.—Effect of temperature on dynamic fatigue life.



FIG. 10.—Rubber vibrated in shear.

$$\% \text{ minimum shear} = \frac{d_{\min}}{T} (100)$$

$$\% \text{ maximum shear} = \frac{d_{\max}}{T} (100)$$

the figure: 0 per cent, 12.5 per cent compression, and 25 per cent extension. The first row corresponds to a -25 to $+25$ per cent shear cycle; the second row, to a 0 to 50 per cent shear cycle; and the third row, to a 75 to 125 per cent shear cycle.

The striking observation about these data is that the results in shear fatigue are entirely in accord with what would have been predicted from the linear fatigue data.

Consider samples *B* and *C*. *B*, vibrated between 0 and 50 per cent shear, had a fatigue life of 1,000,000 cycles. *C*, vibrated between 75 and 125 per cent shear, had a fatigue life of 15,000,000 cycles. The shear oscillation cycle for both samples

was one of 50 per cent. *C* had a much greater fatigue life than did *B*. This is due to the fact that the rubber elements in *C* were in strain at all times during the shear cycle, whereas those in *B* went back to a condition of zero strain once each cycle. Essentially the elements in *C* were working up on the linear extension fatigue hump, whereas those in *B* were being vibrated at the linear fatigue minimum.

In sample *A* the shear cycle was one from -25 to $+25$ per cent, a total shear cycle of 50 per cent. The fatigue life of *A* was seven times that of *B*. Actually *A* was subjected to an alternating 25 per cent shear cycle; once from 0 per cent shear to -25 per cent shear, then once from 0 per cent shear to $+25$ per cent shear. The double 25 per cent shear cycles are essentially two repeated 25 per cent shear cycles. A shear unit of this same 50 durometer stock vibrating through










SHEAR CYCLE	LATERAL STRAIN		
	NONE	12½% COMPRESSION	25% EXTENSION
-25% TO +25%	A  7-MILLION	D  20-MILLION	G  12-MILLION
0% TO 50%	B  1-MILLION	E  2-MILLION	H  2-MILLION
75% TO 125%	C  15-MILLION	F  2-MILLION	I  40-MILLION

FIG. 11.—Dynamic fatigue results on shear samples of 50 durometer stock.

a single shear cycle of 0 to 25 per cent shear has a fatigue life of about 14,000,000 cycles. It is therefore consistent that *A* — each of whose cycles represents two vibrations from 0 to 25 per cent — should last only 7,000,000 cycles.

Sample *D* had a greater life than *A*; *E* had a greater life than *B*. The reason is that the rubber elements were being vibrated essentially with a minimum strain which falls in the compression region and, on the basis of linear fatigue data, *D* and *E* should have the higher fatigue lives. In *F*, however, the dynamic fatigue life was considerably less than in *C*. In *F* the rubber elements which under no shear were under lateral compression were essentially relieved from the compression by the extension resulting from the higher shear; and the rubber elements were being worked in a low dynamic fatigue region near the zero of strain.

Sample *G* had a higher fatigue life than *A*; *G* should have a higher life because the rubber elements were always under extension strain during the vibration. Finally, *I* had a higher dynamic fatigue life than did *C*. The rubber elements in *I* were in higher extension than in case *C*; in other words, the shear strain and

the lateral extension strain essentially added to place the rubber unit in a more favorable fatigue region.

Many theories can be devised to explain the way the dynamic fatigue properties of rubber vary with the strain and the strain oscillation conditions, but such theories are still conjectures.

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MECHANICAL PROPERTIES OF RAW AND VULCANIZED RUBBERS DURING PERIODIC DEFORMATION *

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The construction of an apparatus for measuring the modulus of elasticity and the mechanical losses in raw and vulcanized rubbers during the periodical deformation of compression is described. With the aid of this device it is possible to measure these characteristics at frequencies from 10 to 50 cycles per second for relative compression deformations from 1 to 50 per cent and in a wide range of temperatures. The relation between temperature and modulus of elasticity and mechanical losses was studied at 30 cycles per second for various grades of raw and vulcanized rubbers and a general regularity of this dependence was determined. In the solution of technical problems such as the construction of automobile tire treads, the behavior of rubber under conditions of rapidly changing periodic deformation is highly important. Here the two characteristics of rubber: the dynamic modulus of elasticity and the magnitude of that part of work of deformation which is irreversibly spent during one cycle (mechanical losses) are of the greatest interest. In previous studies of these properties, three basic methods have been used:

(1) Plotting of a curve of the resonance produced by inciting longitudinal vibrations in a sample having the form of a bar;¹

(2) Examination of the frequency relation of the sound absorption in a sample pressed between two membranes, one of which is the source of sound and another the receiver²;

(3) Measurement of the true frequency of longitudinal vibrations and the decrement of fading of vibrations in a bar-shaped sample incited in it by a longitudinal blow³.

All these methods require the use of highly complicated apparatus and comparatively large samples (up to 1 meter), with considerable inconvenience in securing the samples rigidly in the apparatus. The chief shortcoming of these methods is the insignificant deformation amplitude, usually not exceeding 0.1 per cent, whereas in the performance of rubber tires, for example, the relative deformation can exceed 10 per cent.

The object of the present investigation was to develop a simple method for measuring the dynamic modulus and mechanical losses of raw and vulcanized rubbers under conditions approaching those obtained in the practical use of rubber tires:

The construction of the device is based on the idea involved in the well known Schenck apparatus for the determination of elastic hysteresis of metals.

CONSTRUCTION OF APPARATUS AND METHOD OF TESTING

Figures 1a and 1b show a general view and cross-section of the apparatus. In the center of a thin steel beam 1, supported by 2 columns, are fastened a cylindri-

* Translated by Charles Blanc for RUBBER CHEMISTRY AND TECHNOLOGY from the *Journal of Technical Physics* (U. S. S. R.), Vol. 9, No. 4, pages 275-282, 1939.

cal lead weight 2 and a dynamometric ring 3, ending in pointer 4. The latter is an ivory cylinder fitted with a brass cap. The weight is topped by the post 5 in which the eccentric 6 revolves on two ball-bearings. The axis of the eccentric is connected by means of a flexible rubber roller with the axis of a series electric motor, whose speed is regulated by a rheostat. In this way, it is easy to attain motor revolutions resonant with the proper frequency of the system described above. In this case the frequency of vibrations is determined by the elasticity of the beam and the total mass of various parts attached at its center. The amplitude of vibrations depends on the mass of the eccentric and its degree of eccentricity. Changes in the frequency of vibrations are effected stepwise by the use of beams of different thickness. In this way, it is possible to vary the frequency within limits from 10 to 50 Hz. Changes in the amplitude of vibrations in the state of resonance can be effected smoothly because of the special

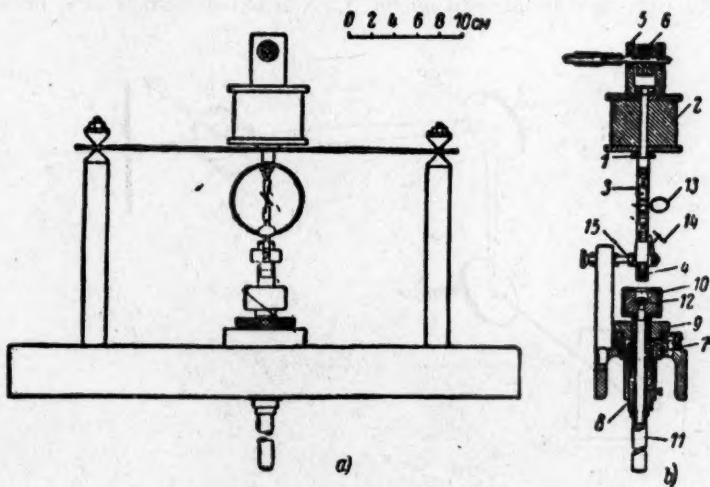


FIG. 1.

construction of the eccentric. The latter consists of two parts, and by turning one part in relation to another the eccentricity and thereby the vibration amplitude of the system can be varied within wide limits.

The stationary unit of the apparatus is installed on the ebonite base 7. The hollow running screw 8 is shifted in a vertical direction by means of the screw nut 9. A copper bar is passed through the hollow of the screw and is fixed in the central position by two ivory bushings. The free space in the hollow between the copper bar and the walls is filled with cork dust. At the top of the copper bar a heavy brass cup 10 is threaded on, and at the bottom a long copper rod 11. A thick woolen cloth is glued to the surface of the cup. The rubber sample 12 to be tested is placed in the cup and, by turning nut 9, the cup is raised until the sample touches the pointer. When motor is set into motion, the sample undergoes periodical deformation of compression, the amplitude of which reaches a maximum at the number of revolutions corresponding with the resonance. By the use of cylindrical samples with a ratio of diameter to height of 1.5, it is possible to obtain relative compression deformations from 0 to 10 per cent in samples 6 mm. high and from 0 to 50 per cent in samples 1 mm. high.

The magnitude of the force applied to the sample is registered with the aid of the mirror 13. The latter is fastened to a steel prism of rhombic section, which is pressed between two thin brass sheets. For greater stability of the mirror, the brass sheets are fitted with scratch dents to fit the sharp ribs of prism. On pressing the dynamometric ring the mirror turns around the axis perpendicular to the plane of the drawing (Figure 1a). The magnitude of compression of the sample is registered with the aid of the mirror 14, which also is fastened to a steel prism. The latter, similar to the prism of the mirror 13, is pressed between two brass plates. One of these plates is tightly connected with the pointer and another with the stationary ring 15. By moving the pointer in the vertical direction, the mirror 14 turns around the axis lying in the plane of the drawing (Figure 1a). Thus, the turning axes of the two mirrors are mutually perpendicular.

A scheme of the optical arrangement of the apparatus is shown in Figure 2. The light from lamp *P*, passing through the diaphragm and system of lenses *L*, falls as a converged beam onto mirror S_1 , is reflected from it onto mirror S_2

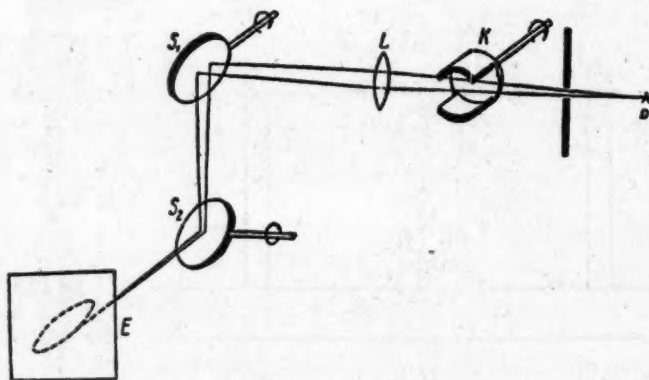


FIG. 2.

and is projected as a visible bright light spot on frosted glass *E* situated in the focus of the system *L*. The compression of the dynamometric ring displaces the visible light spot in the horizontal direction; a shift of the pointer displaces it in the vertical direction. Because the phase of deformation in the compressed sample is retarded in relation to the tension (elastic hysteresis), the visible light spot describes a closed loop on the frosted glass. This loop can be easily traced on a transparent paper or photographed by placing a sensitive plate in place of the frosted glass (see, *e. g.*, Figure 3).

The apparatus is calibrated in the following manner. For the calibration of mirror 13, the top surface of cup 10 is covered with a flat-parallel metallic plate. By turning nut 9, the plate together with the cup is moved upward and is pressed against pointer 4. The pointer is then lifted by hand and a thin calibrated disk is placed in the space between the pointer and the plate. In these operations the visible light spot on the projection screen is somewhat displaced. By repeating this experiment with calibrated disks of different thicknesses, and measuring each time the resulting displacement of light spot along the screen ordinate, it is possible to determine the relation between the displacements of the pointer and the light spot. In our experiments (at a distance between mirror and screen of

45 cm.) a 1-cm. displacement of the light spot along the axis of ordinates corresponded to a 0.0045-cm. displacement of the pointer.

For the graduation of the readings of mirror 14, a special dynamometer is set between the pointer and cup and a sufficiently large load is placed on the post 5. This causes a shift of the light spot on the screen. By repeating this experiment with different loads and comparing each time the resulting displacement of the light spot on the screen along the abscissa with the indications of the special dynamometer, it is possible to determine the relation between the force acting on the pointer and the displacement of the light spot. In our experiments a displacement of 1 cm. of the light spot along the abscissa corresponded to a pressure of 400 grams on the pointer.

The frequency of vibrations is controlled by the stroboscopic method. A blade scoop *K* (Figure 2) is placed in the path of the light beam. The scoop is fastened to the motor shaft, the other end of which is connected with a tachometer.



FIG. 3.

While the motor is revolving, the blades periodically interrupt the light beam. It can be readily seen that at a number of motor revolutions equal to the frequency of vibrations of the installation, two breaks in the light beam will take place during one full cycle and accordingly the image of the loop on the screen will be broken into two parts. By varying the number of motor revolutions with the aid of a rheostat, it is easy to obtain this picture. In this case the frequency of vibrations is directly proportional to the readings of tachometer.

For measurements below room temperature, the copper rod 11 (Figure 1) is immersed in liquid air in a Dewar flask. In this way, sample 12 in the cup, connected with the copper rod, is indirectly cooled. By varying the depth of immersion in liquid air, it is easy to regulate the rate of cooling of the cup and to maintain the sample at constant temperature. For experiments above room temperature, instead of cup 10 use is made of a special cup wound with a few strands of Nichrome wire. An electric current is passed through the wires and the temperature is regulated with the aid of a connecting rheostat. The rate of the temperature regulation of the sample is controlled by means of two thermo-

couples, one of which is inserted inside the sample and another is soldered to the cup. At a rate of cooling (or heating) of the cup equal to 5° C. per minute, the readings of the two thermocouples were exactly identical. Therefore in all the subsequent experiments only the temperature of the cup was measured, whereby the speed of cooling (or heating) never exceeded 4° C. per minute.

It was shown above that, in the deformation of rubber, a shift of phases between the force and deformation takes place. This causes the beam of light to describe a closed loop on the projection screen. Since the elastic system which causes the deformation of a sample varies consistently, then:

$$S = S_m e^{i(\omega t - \theta)} \quad (1a)$$

$$P = P_m e^{i\omega t} \quad (1b)$$

where S and P are the instantaneous values of deformation and force, respectively, S_m and P_m are the amplitudes of deformation and force, and θ is the angle of the shift of phases between the force and deformation.

From formula (1) it follows that the hysteresis loop must have the elliptic form, the area of which is equal to:

$$Q = \pi \cdot P_m \cdot S_m \sin \theta \quad (2a)$$

The magnitude of this area, expressed in gram per cm., is equal to the irreversible work expended in deforming the sample through one cycle.

It is natural to choose the value of $\sin \theta$ as a characteristic of the mechanical losses in a sample, and it can be determined from the equation:

$$\sin \theta = \frac{1}{\pi} \frac{Q}{P_m S_m} \quad (2b)$$

From Figure 4 it is evident that $\sin \theta$ is equal to the ratio, multiplied by $4/\pi$, of the loop area to the area of the rectangle described around the loop.

Further it can be shown that:

$$\frac{dS}{dP} = \frac{S_m}{P_m} (\cos \theta - i \sin \theta) \quad (3)$$

For a cylindrical sample 1 cm. high and 1 sq. cm. in diameter:

$$dS/dP = 1/E,$$

where E is the modulus of elasticity.

Thus, the reciprocal of the modulus of elasticity, is expressed by the complex figure:

$$1/E = 1/E_1 - i1/E_2 \quad (3a)$$

As a characteristic of the elastic properties of a material, the value of the material part of this expression may reasonably be accepted:

$$\frac{1}{E_1} = \frac{S_m}{P_m} \cos \theta \quad (4)$$

From Figure 4 it is evident that $1/E_1$ is equal to the ratio of the deformation in elapsed time $t = n\pi\omega$ to the amplitude of the force P_m . In the following lines magnitude $1/E_1$ will be called "coefficient of elasticity" and will be represented by γ . The magnitude $1/\gamma$ will be called the "modulus of elasticity" and will be designated by E .

Measurements of the coefficient of elasticity (γ) and $\sin \theta$ were carried out in the following way. A sample of the material, in the form of a cylinder, is placed in cup 10 and then pressed by the pointer. The required temperature of the sample is regulated by the method described in paragraph 5. The resonance position, corresponding to the maximum size of the loop on the projection screen, is determined by starting the motor, which revolves the eccentric δ , and operating the rheostat (set in the circuit of the motor). The screen is covered with a sheet of transparent paper, and the axes of the screen coördinates (previously indicated on the frosted glass) and the loop itself are traced on the paper. On the same paper a drawing is made of the rectangle, the sides of which, are parallel to the axes of coördinates, and therefore are tangent to the loop. Between the two points of tangency to the sides of the rectangle a straight line is drawn parallel to the coördinate axes (of deformation) (Figure 4). The drawing is placed in a photographic camera and is projected on a white paper at a magnification of 2-3. The area of loop Q_1 and that of rectangle Q_2 described around the loop are

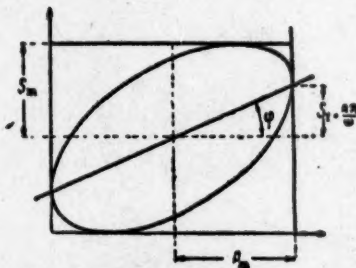


FIG. 4.

measured with a planimeter; $\tan \phi$ is determined with a common rule. Finally, $\sin \theta$ and γ (see paragraph 6) are calculated from these data:

$$\sin \theta = \frac{4}{\pi} \cdot \frac{Q_1}{Q_2}, \quad (5)$$

$$\gamma = \tan \phi \cdot \frac{a}{b} \cdot \frac{\pi}{4} \cdot \frac{d^2}{h}, \quad (6)$$

where a is the relation between the displacement of the pointer and the displacement of the light spot on the screen along the coördinate axes (see paragraph 3); b is the relation between the force (in grams) pressing on the pointer and the displacement (in centimeters) of the light spot on the screen along the abscissa.

Control tests of the deviations of $\sin \theta$ and γ revealed that, within the limits of not too large relative deformations (up to 10 per cent), $\sin \theta$ and γ are independent of the size of the sample and do not practically vary with changes in the degree of compression (from 5 to 20 per cent), in the amplitude of deformation (from 3 to 10 per cent) and in the frequency (from 25 to 35 cycles per second). Within these intervals, the measurements of $\sin \theta$ and γ of the same sample do not vary more than 5 per cent from the mean values. In measurements of different samples of the same material the deviations in $\sin \theta$ lie also within the limits of ± 5 per cent, while the errors in the determination of γ increase to ± 15 per cent. The latter discrepancy must be ascribed to the inaccuracy of the linear measurements of the samples.

THE EXPERIMENTAL RESULTS AND DISCUSSION

To check the methods of measurement and to obtain data on the properties and behavior of raw and vulcanized rubbers under periodic deformation, it was of interest to investigate the functional relations of $\sin \theta$ and γ to temperature for a number of different materials. The materials and their basic characteristics are given below:

- (1) Compound from natural rubber with 3 per cent of sulfur (see Figure 5)
 - (a) Vulcanized 20 minutes at 2 atm. pressure
 - (b) Vulcanized 70 minutes at 2 atm.
- (2) Compound from sodium-bivinyll rubber (plasticity 0.5) with 2.5 per cent of sulfur (Figure 6)
 - (a) with no lampblack
 - (b) with 25 per cent of lampblack
 - (c) with 50 per cent of lampblack
- (3) Chloroprene Compounds (Figure 7)
 - (a) Raw rubber
 - (b) Vulcanized rubber
- (4) Sodium-bivinyll rubber (Figure 8)
 - (a) Common
 - (b) Resistant to freezing
- (5) Ebonite prepared from sodium-bivinyll rubber with 40 per cent of sulfur (Figure 9)
- (6) Raw sodium-bivinyll rubber (Figure 10)
 - (a) Plasticity 0.62
 - (b) Plasticity 0.51
 - (c) Plasticity 0.33
 - (d) Plasticity 0.23
- (7) Raw natural rubber (smoked sheet) (Figure 11)
 - (a) Stored a long time after milling
 - (b) Milled before the experiment

Samples of these materials were shaped in the form of a cylinder measuring 6 mm. high and 8 mm. in diameter. The amplitude of relative deformation in different experiments varied from 1 to 10 per cent. The vibration frequency was 30 ± 5 cycles per second. The dynamic modulus and mechanical losses as functions of temperature were examined for each of the above materials. The experimental results are shown in Figures 5, 6, 7, 8, 9, 10 and 11, where the temperature (Centigrade) is plotted as abscissa, and $\sin \theta$ (on the left) and γ in sq. mm. per kg. (on the right) as ordinate. The points on the curves of γ are marked by small tails.

From the graphs (Figures 5 to 11) it is evident that the temperature relations of $\sin \theta$ and γ are qualitatively similar for a wide range of polymeric substances from raw rubber to ebonite. It should be pointed out that the dependence of $\sin \theta$ and γ on temperature resembles closely the temperature relationships of the dielectric losses and dielectric constants of amorphous and polymeric substances. This indicates a close connection between the phenomena of mechanical and electric relaxation. The temperature corresponding to the maximum $\sin \theta$ as well as the temperature at the point of flexure of the curve of γ are, generally speaking, different for different polymers.

With the aid of the graphic data (Figures 5 to 11) it is possible to obtain information on the influence of the structure of polymers on the temperature corresponding to $\sin \theta_{\max}$ and $\gamma_{\text{curvature}}$.

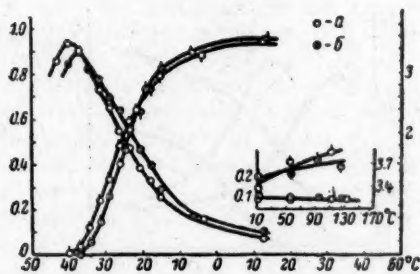


FIG. 5.

- (a) Vulcanized 20 min. at 2 atm.
(b) Vulcanized 70 min. at 2 atm.

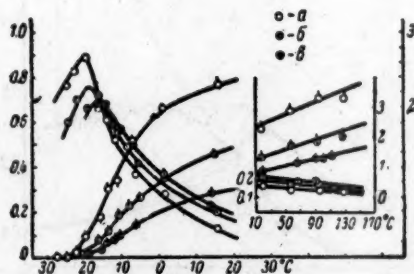


FIG. 6.

- (a) 0% lampblack.
(b) 25% lampblack.
(c) 50% lampblack.

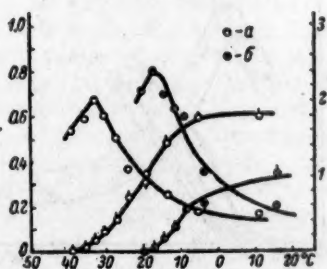


FIG. 7.

- (a) Raw rubber.
(b) Vulcanized rubber.

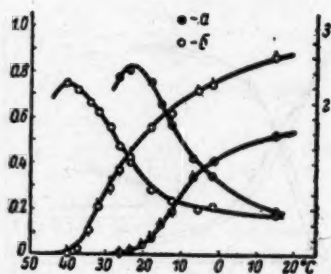


FIG. 8.

- (a) Rubber composition of usual formula.
(b) Rubber resistant to freezing temperature.

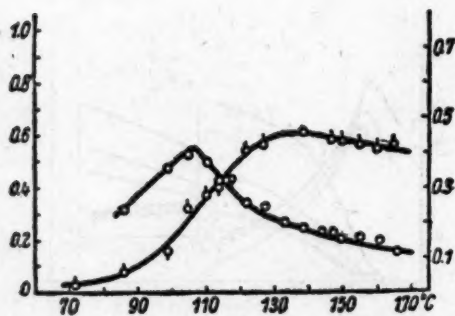


FIG. 9.

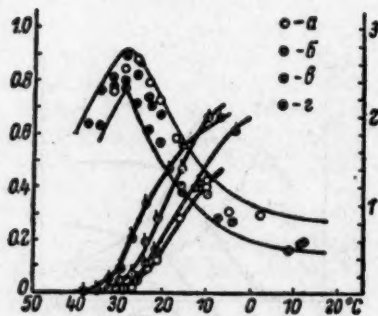


FIG. 10.

- (a) Plasticity 0.62%.
(b) Plasticity 0.51%.
(c) Plasticity 0.33%.
(d) Plasticity 0.28%.

A comparison of the results obtained with chloroprene rubber and vulcanized rubber, which are known to differ in their degrees of polymerization, shows that the curves of $\sin \theta$ and γ are shifted toward the region of higher temperatures with increase in the degree of polymerization, i. e., with the change from raw rubber to vulcanized rubber (Figure 7).

A comparison of Figure 6 (vulcanized rubber with 2.5 per cent of combined sulfur) with Figure 9 (vulcanized rubber with 40 per cent of combined sulfur, i. e., ebonite) shows that, with increase in the degree of vulcanization, the curves of $\sin \theta$ and γ are shifted toward the region of higher temperatures.

Solid fillers (lampblack) from 0 to 50 per cent do not change significantly the temperature of the maximum of $\sin \theta$ or the curvature of γ (Fig. 6).

Some ingredients in rubber cause a considerable shift in the temperature of the maximum value of $\sin \theta$ and that of the curvature of γ toward the region of lower temperatures (Figure 8).

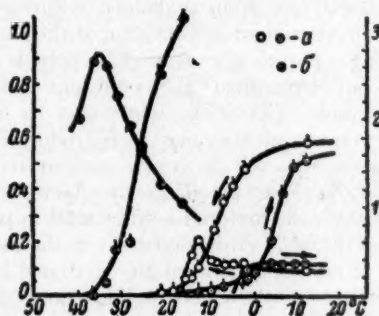


FIG. 11.

(a) Raw rubber stored long time after milling.
(b) Raw rubber freshly milled.

In conclusion attention should be called to the interesting process which takes place in milled natural raw rubber (smoked sheet) after prolonged storage at room temperature. A sample thus treated was placed in the apparatus and cooled at the rate of 4°C to -25°C and then heated at the same rate to room temperature. In the process of cooling and heating, a hysteresis loop was drawn at intervals of a few degrees of temperature. The results of this experiment are shown in Figure 11(a). The graph shows that the changes in $\sin \theta$ and γ during cooling differ from the changes during heating, as if the rubber did not succeed in thawing in time. This phenomenon is characteristic only for natural raw rubber stored for a long time after milling. Freshly milled natural raw rubber, as well as all the other materials tested, did not display any difference in the temperature course of $\sin \theta$ and γ on cooling or heating.

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- ⁴ Here and in the following lines, S and P denote the differences $S-S_0$ and $P-P_0$, where P_0 and S_0 are the force and deformation, respectively, corresponding to preliminary compression of the sample.

MEASURING THE PERMEABILITY OF RUBBER TO VARIOUS GASES *

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Considerable difficulty has been experienced in assessing the ability of sheets of rubberlike materials to resist permeation by gases. The slowness of the process in the most important case of the "permanent" gases necessitates special experimental conditions to give a comparatively great permeation rate, and so introduces several factors which tend to decrease the trustworthiness of the results. Among the difficulties introduced may be mentioned the preparation of suitable test-pieces (thin, uniform sheets free from pinholes), accurate temperature control of bulky apparatus, the prevention of deformation of the sheets, and the measurement of the quantities of gas passed after reasonable periods of time. Moreover, in investigations which do not approximate the conditions under which the material is to be employed in practice, interfering factors may be introduced which may make results worthless even though they may be reproducible. For example, when the experimental conditions are such as to give comparatively rapid permeation rates, rate of solution and of evaporation of gas may be influential factors, whereas under the conditions in which the material is to be used in practice, the governing factor may be the rate of diffusion of dissolved gas in the material.

The indirect method of assessing permeability, outlined below, overcomes in a large measure the difficulties of the direct method, and also gives independent values for the two factors which are shown to govern permeability.

DIFFUSION OF GASES

Gases are soluble in rubberlike substances. When such substances are placed in a gas, solution takes place at the surfaces and dissolved gas diffuses into the interior. If the gas pressure is maintained constant or allowed to become constant, an equilibrium is attained at which dissolved gas is uniformly distributed throughout the material. This saturation concentration depends on the chemical nature of the solute and of the solvent, on the temperature, and on the gas pressure. If, after equilibrium has been attained, the gas pressure is changed isothermally and maintained at a new value, gas dissolves or evaporates at the surface, according, respectively, as the new pressure is greater or less than the original pressure, and diffusion takes place in the body of the solvent material until a new equilibrium is reached at which dissolved gas is once more uniformly distributed and at the saturation concentration corresponding with the new gas pressure. We may regard the dissolution of free gas, or the evaporation of dissolved gas in an infinitesimally thin layer, as occurring instantaneously with change of gas pressure, and assume the gas dissolved in the surface layer to be always in equilibrium with the external gas. As, however, in the interior of the solvent material (as distinct from the infinitesimally thin surface layer) change of concentration can take place only by the movement of dissolved gas by diffusion under a concentration gradient, the concentration of gas in the interior is a function of time.

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When a solute is not uniformly distributed throughout a solvent medium, the change of concentration which takes place at any point due to diffusion is given by the Fick's law relationship:

$$\frac{\partial c}{\partial t} = k \left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right] \quad (1)$$

where

c = concentration

t = time

k = diffusion constant

x, y and z = coördinates of the point with respect to rectangular axes

The diffusion constant is defined by the fundamental diffusion relationship

$$dQ = -k \times A \times \frac{dc}{dl} \times dt \quad (2)$$

where

Q = quantity of solute

l = distance

A = cross-section area perpendicular to the direction in which l is measured; its dimensions are (length)² (time)⁻¹

The diffusion constant is characteristic of any pair of substances, solute and solvent, and depends on temperature. Justification for the assumption of Equations 1 and 2, that the diffusion constant is independent of the actual concentration, is given below.

PERMEATION THROUGH A UNIFORM SHEET

The mechanism of permeation here described, involving solution, diffusion and evaporation, has been clearly indicated by Daynes.¹ Consider a sheet of a rubber-like substance, of uniform thickness, L , and cross-sectional area, A , separating two reservoirs of gas maintained at different constant pressures, p_1 and p_2 . Gas dissolves at the surfaces and diffuses into the interior. No static equilibrium can be reached as the saturation gas concentrations, corresponding with the two gas pressures, are maintained in the respective faces and a constant concentration difference is maintained between them. A dynamic equilibrium will, however, be attained at which gas passes through the sheet at a constant rate.

We may assume Henry's law and write $c = hp$, where p = gas pressure, c = equilibrium gas concentration in the material—i. e., the solubility at gas pressure p —and h = proportionality constant characteristic of the solute and solvent. The simpler diffusion Equation 2 may be applied and used to show, first, that

$$c = c_1 + \frac{l}{L} (c_2 - c_1)$$

where c is the gas concentration at a point distant l from the face in contact with the gas at pressure p_1 , and c_1 and c_2 are the equilibrium gas concentrations corresponding with gas pressures p_1 and p_2 , respectively, i. e., $c_1 = hp_1$ and $c_2 = hp_2$, that is, the concentration varies linearly with distance from one face. Secondly, it can be deduced that

$$Q = -k A \frac{h(p_2 - p_1)}{L} t \quad (3)$$

In this relationship, the factors characteristic of the materials are k and h , and with standardized experimental conditions we may write

$$Q = (\text{constant}) \times kh \quad (4)$$

Or, in a comparison of the resistance offered by sheets of materials to the passage of gases,

$$Q_a : Q_b : Q_c \dots :: k_a h_a : k_b h_b : k_c h_c \dots$$

where $Q_a, Q_b, Q_c \dots$ are the quantities of the gases passing, and $k_a h_a, k_b h_b, k_c h_c \dots$ are the corresponding products of the diffusion constant and the Henry's law constant for the corresponding combinations of rubberlike substance and gas.

ABSORPTION BY A BLOCK

Considering now the change in the total quantity of gas dissolved in a solid block of rubberlike material, when after attaining equilibrium in the gas at one

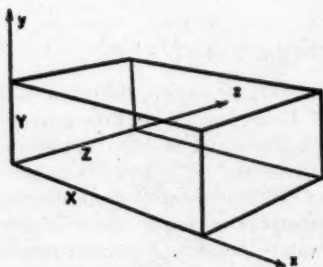


FIG. 1.—Block.

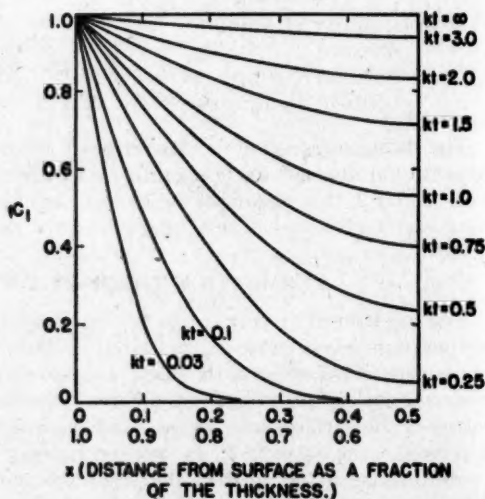


FIG. 2.—Variation of fractional concentration of gas in a sheet with distance from surface.

pressure, the pressure is instantaneously and isothermally changed and maintained at a new value, the total quantity of gas, q , dissolved at any time is given by

$$q = \iiint c \times dx \times dy \times dz \quad (5)$$

where c , the concentration of gas dissolved in the element of volume $dx \times dy \times dz$ at the point x, y, z , is given by the Fick's law relationship, Equation 1. It is possible, under the above conditions of gas pressure, and limiting consideration to certain geometric shapes for the block of material, to integrate the Fick's law equation and evaluate c as a function of the product kt and x, y , and z , and further, to carry out the integrations to determine q as a function of kt and of the dimensions of the block of material.

The particular geometric shape of the block which we consider here (Figure 1) is that of a right-rectangular prism of dimensions X, Y and Z , and we discuss

the three particular cases in which (1) two pairs of opposite faces are impermeable, the pair of faces of dimensions YZ only being permeable; (2) one pair of opposite faces is impermeable, the two pairs of faces of dimensions YZ and XZ only being permeable, and (3) all six faces are permeable.

The condition of impermeability, or negligible permeability, is easily experimentally realized either by the obvious method of the application of impermeable coatings, *e. g.*, of tinfoil, by means of a suitable adhesive, or by employing test-pieces the dimensions of which are great in certain directions—for example, case 1 is met by employing a sheet of relatively thin material of great area and case 2 by a rectangular-sectioned prism of great length.

In the first case, diffusion of dissolved gas may be regarded as taking place in one direction only (parallel to the axis of x); in the second case, in two directions at right angles (parallel to the axes of x and y); and in the third case, in three directions at right angles (parallel to the axes of x , y , and z). In spite of the simplicity of these conditions, in no case is it possible to obtain a simple expression for c , the concentration of gas at the point x, y, z , from the Fick's law equation; solutions can, however, be obtained in series form. These may be written

$$C_1 = \frac{c - c_0}{c_\infty - c_0} = 1 - \frac{4}{\pi} \sum \frac{1}{n} e^{-kn^2 \frac{\pi^2}{X^2} t} \sin n \frac{\pi}{X} x \quad (6)$$

$$C_2 = \frac{c - c_0}{c_\infty - c_0} = 1 - \frac{16}{\pi^2} \sum \frac{1}{mn} e^{-k \left(m^2 \frac{\pi^2}{X^2} + n^2 \frac{\pi^2}{Y^2} \right) t} \sin m \frac{\pi}{X} x \times \sin n \frac{\pi}{Y} y \quad (7)$$

$$C_3 = \frac{c - c_0}{c_\infty - c_0} = 1 - \frac{64}{\pi^3} \sum \frac{1}{lmn} e^{-k \left(l^2 \frac{\pi^2}{X^2} + m^2 \frac{\pi^2}{Y^2} + n^2 \frac{\pi^2}{Z^2} \right) t} \sin \frac{\pi}{X} x \times \sin m \frac{\pi}{Y} y \times \sin n \frac{\pi}{Z} z \quad (8)$$

where l, m and n are positive odd integers; c_0 = concentration of gas in the block at equilibrium under the original gas pressure, *i. e.*, the uniform concentration at zero time, c_∞ = concentration of gas in the block at equilibrium under the new gas pressure, *i. e.*, the uniform concentration after infinite time— C_1, C_2 , and C_3 are the fractional increases in concentration at the point (x, y, z) in cases 1, 2, and 3, respectively. The summations may be carried out by assuming particular values for the product kt and for x, y and z . For example, the fractional increase in gas concentration after a time t_1 , at points one quarter of the way through a sheet of material, *i. e.*, $x = \frac{X}{4}$, in which the diffusion constant of the gas is k_1 , *i. e.*, $kt = k_1 t_1$, is given by

$$C_1 = 1 - \frac{4}{\pi} \left[\frac{1}{1} e^{-1^2 \frac{\pi^2}{X^2} k_1 t_1} \sin \frac{\pi}{4} + \frac{1}{3} e^{-3^2 \frac{\pi^2}{X^2} k_1 t_1} \sin 3 \frac{\pi}{4} + \frac{1}{5} e^{-5^2 \frac{\pi^2}{X^2} k_1 t_1} \sin 5 \frac{\pi}{4} + \dots \right]$$

The series is rapidly convergent and can be summed by evaluating the first few terms. Figure 2, which was derived in this way, shows the gas concentration at all points through a sheet after several time intervals.

The quantities of gas absorbed at any time are obtained from relationships 6, 7 and 8 by integration (see Equation 5), the results again being in series form. They may be written:

$$Q_1 = \frac{q - q_0}{q_\infty - q_0} = 1 - \frac{8}{\pi^2} \sum \frac{1}{n^2} e^{-kn^2 \frac{\pi^2}{X^2} t} \quad (9)$$

$$Q_2 = \frac{q - q_0}{q_\infty - q_0} = 1 - \frac{64}{\pi^4} \sum \frac{1}{m^2 n^2} e^{-k \left(m^2 \frac{\pi^2}{X^2} + n^2 \frac{\pi^2}{Y^2} \right) t} \quad (10)$$

$$Q_3 = \frac{q - q_0}{q_\infty - q_0} = 1 - \frac{512}{\pi^6} \sum \frac{1}{l^2 m^2 n^2} e^{-k \left(l^2 \frac{\pi^2}{X^2} + m^2 \frac{\pi^2}{Y^2} + n^2 \frac{\pi^2}{Z^2} \right) t} \quad (11)$$

where l , m and n are positive odd integers; q_0 = quantity of gas in the block at equilibrium under the original gas pressure, i. e., at zero time— q_∞ = quantity of

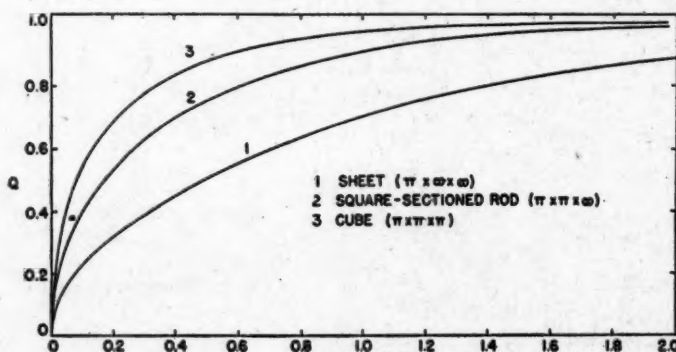


FIG. 3.—Variation of fractional quantity of gas absorbed by sheet, square-section rod, and cube with time.

gas in the block at equilibrium under the new gas pressure, i. e., after infinite time, and Q_1 , Q_2 , and Q_3 are the fractional increases in the quantities of gas absorbed in cases 1, 2, and 3, respectively. The summations may be carried out by assuming particular values for the product kt . For example, the fractional increase in the quantity of gas absorbed after a time t_1 by a sheet of material in which the diffusion constant of the gas is k_1 , i. e., $kt = k_1 t_1$, is given by

$$Q_1 = 1 - \frac{8}{\pi^2} \left[\frac{1}{1^2} e^{-1^2 \frac{\pi^2}{X^2} k_1 t_1} + \frac{1}{3^2} e^{-3^2 \frac{\pi^2}{X^2} k_1 t_1} + \frac{1}{5^2} e^{-5^2 \frac{\pi^2}{X^2} k_1 t_1} + \dots \right]$$

The series is rapidly convergent and can be summed by evaluating the first few terms.

It is to be noted that Q_1 , Q_2 and Q_3 are independent of q_0 , q_∞ , k and t and depend only on x , y , z and the product kt . That is, two identical blocks of materials in which the diffusion constants of the gases are k_1 and k_2 reach the same degree of fractional saturation after times t_1 and t_2 which bear the relation $t_1/t_2 = k_2/k_1$.

Relationships 9, 10 and 11 may be simplified, as may also 6, 7 and 8, by considering test-pieces the dimensions of which are equal in the directions in which diffusion takes place and by choosing units of length such that these dimensions are equal to π units; or, in other words, by considering, for example, (1) an infinite sheet of thickness π units of length ($X=\pi$); (2) an infinite rod of square cross-section $\pi \times \pi$ (units of length)², ($X=Y=\pi$); and (3) a cube, $\pi \times \pi \times \pi$ (units of length)³, ($X=Y=Z=\pi$).

Relationships 9, 10, and 11 reduce to:

$$Q_1 = 1 - S \quad (12)$$

$$Q_2 = 1 - S^2 \quad (13)$$

and

$$Q_3 = 1 - S^3 \quad (14)$$

where

$$S = \frac{8}{\pi^2} \sum \frac{1}{n^2} e^{-n^2 kt}$$

and n is a positive odd integer.

Table I gives the values of Q_1 , Q_2 and Q_3 for a range of values of kt ; it also includes the values of $\frac{Q_1^2}{kt}$ for these values of kt . It is seen from the table that, up to a value of about 0.6 for Q_1 , the value of $\frac{Q_1^2}{kt}$ remains substantially constant. This is a purely empirical relationship. Figure 3 gives the values of Table I plotted graphically. This constancy of $\frac{Q_1^2}{T}$ in the experimental results

TABLE I
QUANTITIES OF GASES ABSORBED

kt	Q_1	Q_2	Q_3	$\frac{Q_1^2}{kt}$
0.05	0.4606	0.2954	0.4087	0.51600
0.1	0.2272	0.4027	0.5383	0.51600
0.15	0.2782	0.4790	0.6240	0.51601
0.2	0.3214	0.5393	0.6873	0.51602
0.25	0.3592	0.5876	0.7369	0.51602
0.3	0.3934	0.6321	0.7769	0.51600
0.35	0.4249	0.6691	0.8097	0.51599
0.4	0.4542	0.7021	0.8374	0.51574
0.45	0.4816	0.7314	0.8607	0.51538
0.5	0.5074	0.7573	0.8805	0.51484
0.55	0.5317	0.7807	0.8973	0.51402
0.6	0.5547	0.8016	0.9117	0.51290
0.65	0.5766	0.8207	0.9241	0.51147
0.7	0.5973	0.8378	0.9347	0.50970
0.75	0.6170	0.8533	0.9438	0.50760
0.8	0.6357	0.8673	0.9516	0.50517
0.85	0.6535	0.8801	0.9584	0.50248
0.9	0.6704	0.8914	0.9642	0.49940
0.95	0.6865	0.9017	0.9692	0.49609
1.0	0.7018	0.9119	0.9738	0.49252
1.2	0.7559	0.9404	0.9854	0.47611
1.4	0.8001	0.9600	0.9920	0.45726
1.6	0.8363	0.9732	0.9956	0.43717
1.8	0.8660	0.9820	0.9976	0.41665
2.0	0.8903	0.9880	0.9987	0.39632
2.5	0.9335	0.9956	0.9997	0.34854
3.0	0.9596	0.9984	—	0.30697
3.5	0.9755	0.9994	—	0.27189
4.0	0.9852	0.9998	—	0.24263

of investigations covering only an initial fraction of the absorption has led to an erroneous assumption that this law applies over the whole absorption period; the continued absorption over long periods implied by this assumption has been explained as being due to swelling.⁶

All the foregoing considerations have been based on the assumption that the diffusion constant is independent of concentration. This assumption is justified on two grounds. In the first place, diffusion arises out of the molecular movement, and the diffusion law, stated in Equation 2, is a necessary consequence of the kinetic theory, assuming only that there is no mutual interference between the diffusing molecules, *i. e.*, assuming conditions comparable with those under which the gas laws may be applied to solutions. In the case of the "permanent" gases with which we are here primarily concerned, the solubilities are so low under all normal conditions of gas pressure and temperature as to be well within the range of noninterference between their molecules. For example, soft rubber at 30° C. dissolves about 5.5×10^{-2} cc. of nitrogen measured at normal temperature and pressure per cc., per atmosphere pressure. The saturation concentration of nitrogen, therefore, at 30° C. under a pressure of 3 atmospheres (the highest pressure which would normally be met with in practice) is 0.0074 gram molecule per liter. In the second place, there is ample experimental evidence that the solubility of gases in rubberlike substances obeys Henry's law^{2, 5, 7}; furthermore, the available experimental evidence shows that permeation rates are proportional to pressure difference^{1, 4}. It is readily realized that these conditions necessitate the independence of the diffusion constant of concentration.

APPLICATION OF ABSORPTION EXPERIMENTS TO MEASUREMENT OF PERMEABILITY

Relationships 12, 13 and 14 show that in all cases the fractional increase in the quantity of gas absorbed depends only on the product of the diffusion constant and time. Furthermore, the total quantity of gas absorbed at equilibrium is independent of the diffusion constant and of time. Therefore experimental results giving the relationship between the quantity of gas absorbed and time can be used to evaluate k and h independently and hence to evaluate the product, kh , which has been shown to be directly proportional to permeability.

We assume the availability of experimental means (detailed below) of determining the q/t relationship and outline methods of determining k and h .

If the change in the total quantity of gas absorbed after infinite time, *i. e.*, at saturation, is q_s :

$$q_s = q_\infty - q_0 = v(c_\infty - c_0) = v(p_2 - p_1)h$$

where v is the total volume of the solvent material, and hence:

$$h = \frac{q_s}{v(p_2 - p_1)}$$

the units depending on those used to measure quantity of gas and gas pressure.

For the evaluation of the diffusion constant, the experimental times (T_1, T_2, T_3 , etc.) to reach any selected, suitable values of the fractional increase in the quantity of gas absorbed are compared with the corresponding values of the product kt (k_1t_1, k_2t_2, k_3t_3 , etc.), deduced from the appropriate theoretical relationships 12, 13 or 14. This is most conveniently carried out by means of the graph of Figure 3. The corresponding values of T and kt are equated to give values for

k (these should be identical) and an average is taken. The following points have, however, to be borne in mind. The dimensions of the diffusion constant are $(\text{length})^2 (\text{time})^{-1}$ and when corresponding values of T and kt are equated the units of time for the resulting value of the diffusion constant are the same as those used in measuring T . The units of length have already been chosen such that the dimensions of the test-piece, measured in the direction in which diffusion takes place, are π units. If these dimensions, measured in the ordinary units, are a cm., the value of the diffusion constant deduced as above must be multiplied by $(a/\pi)^2$ to give its value with centimeters as the units of length.

This method of determining k may conveniently be modified in the following way. It has been shown (Table I) that the value of $\frac{Q_1^2}{kt}$ remains substantially constant ($=\rho$) up to a value of about 0.6 for Q_1 . In the experimental results, the value of $\frac{Q_1^2}{T}$ should also be constant ($=\sigma$) up to this value of Q_1 . (Experimental variation may be overcome by averaging in any convenient manner.) The value of k is therefore obtained by eliminating Q_1 from

$$\frac{Q_1^2}{kt} = \rho$$

and

$$\frac{Q_1^2}{T} = \sigma$$

to give

$$\frac{kt}{T} = \frac{\sigma}{\rho}$$

and if k is measured with centimeters as the units of length and the same units of time as in the experimental procedure (say seconds):

$$k = \frac{\sigma}{\rho} \left(\frac{a}{\pi} \right)^2 \text{ sq. cm. per second}$$

Table I shows that if a value of 0.514 is taken for ρ , the error, for values of Q_1 up to about 0.6, is less than 1 per cent.

If the experimental results have been obtained under conditions which allow diffusion to take place in more than one direction, use may be made of the relationships:

$$Q_1 = 1 - (1 - Q_2)^{1/2}$$

and

$$Q_1 = 1 - (1 - Q_3)^{1/3}$$

in order that this method may be employed to determine k .

In connection with the alteration of the numerical value of k with adjustment of the units of length, a point which arises is the theoretical comparison of the absorption of gas by specimens of different essential dimensions. We consider here only the cases of sheets of great area relative to their thicknesses, of square-sectioned prisms of great length relative to their cross-sectional dimensions, and of cubes. Equations 9, 10, and 11 are modified to

$$Q_t = 1 - \left[\frac{8}{\pi^2} \sum \frac{1}{n^2} e^{-n^2 k \left(\frac{\pi}{a} \right)^2 t} \right]^4$$

where $i=1, 2$, or 3 according, respectively, as diffusion of dissolved gas takes place in one direction only, or in two or three directions at right angles and where k is the value of the diffusion constant with the same units of length which are used to measure a , the dimensions of the test-piece in the direction or directions in which diffusion takes place. Figure 4 shows the variation of the fractional quantity of a gas absorbed by uniform sheets of different thicknesses. In this graph, one particular thickness is chosen for reference and the thicknesses of the other sheets are given as multiples (λ) of this thickness. The curves are all on the same scale, the factor $\frac{1}{\lambda^2}$ being necessary in the abscissas in order to retain a constant absolute value for k with various thicknesses of specimen.

APPLICABILITY OF METHOD TO NONHOMOGENEOUS RUBBERLIKE PRODUCTS

One of the most common and most obvious methods for reducing the permeability of sheets of rubberlike materials to gas is compounding with finely divided inert substances such as clay, whiting and barytes. The reduction of permeability by the incorporation of these substances may be considered as arising out of at least two separable effects. First, they replace some of the solute material and thus reduce the cross-sectional area through which gas may pass; secondly, they cause the gas to take a devious path and so increase the effective thickness.

Considering the first effect, it can be shown that if a fractional volume, θ , of the continuous medium is replaced by uniformly dispersed particles, the fractional area of any cross-section occupied by the particles is also θ . This result is independent of particle shape or size, provided only that the numbers of particles in the volume and area considered are sufficiently great to allow the law of averages to apply. If, therefore, a sheet through which gas is permeating contains a fractional volume of filler θ , the effective area through which gas is passing is reduced to a fraction $(1-\theta)$ of the total area and the permeability is reduced by this effect to a fraction $(1-\theta)$ of that of the corresponding sheet containing no filler. As the solubility per unit volume of the mixture is also reduced to a fraction $(1-\theta)$ of the original value by the introduction of the filler, it is seen that in assessing permeability by absorption experiments, the reduction due to this effect is quantitatively allowed for in the reduced Henry's law constant.

The second effect of fillers, the increased effective thickness of the sheet, is less readily assessed, as particle shape and orientation have to be taken into account. If, however, we regard the reduction of permeability by this effect as arising not out of increased effective sheet thickness, but out of a reduced diffusion constant, it is readily seen that the diffusion constant obtained from permeation experiments, although having no exact physical interpretation, can be applied quantitatively to the assessment of permeability of sheet material, provided only that in the case of anisometric filler particles, their orientation with respect to the direction or directions in which diffusion takes place in the absorption experiments is the same as that of permeation under service conditions. On account of this provision it is preferable, in the absorption experiments, to cut sections from the sheet material and to allow diffusion to take place only in the appropriate direction.

A third possible effect of fillers arises out of experimental results given below (Table IV). With diatomite-compounded rubber mixings the solubility of nitrogen in the rubber (as opposed to the mixing) decreases with increasing proportions of diatomite (see Table II).

Rubber removed by adsorption is calculated from the relative solubility values assuming that adsorption of rubber by diatomite provides a complete explanation for the irregularity in solubility values.

It is suggested that the diatomite may remove some of the rubber from the rubber phase by adsorption, so that it is not free to dissolve gas. The reduction of permeability by diatomite will, therefore, be greater than that anticipated from the volumes of filler incorporated, owing to the effective reduction in the quantity of available rubber and the corresponding increase in particle size of the diatomite.

Barytes does not show a similar adsorption effect. On the other hand, the incorporation of carbon black in rubber mixings increases the solubility of gases by adsorption of gas and this method of measuring permeability cannot be applied, without further consideration, to rubberlike substances compounded with carbon black.

TABLE II
DIATOMITE-COMPOUNDED RUBBER
(Vulcanization, 1 hour at 150° C.)

	Dia- tomite	Relative solubility ^a	Rubber removed by adsorption	
			% ^a	Gram ^b
Rubber	100			
Sulfur	3	0	0	—
Zinc oxide	5	20	8	0.40
Stearic acid	2	40	12	0.30
Nonox	1	60	18	0.30
Mercaptobenzothiazole	1	80	24	0.30
Diatomite	—	100	31	0.31

^a In total rubber.

^b Per gram of diatomite.

APPARATUS AND EXPERIMENTAL PROCEDURE

The authors have devised several forms of apparatus for following the absorption or desorption when the gas in which a test-piece of specified shape is immersed is subjected to a pressure increase or decrease. Those found most convenient of manipulation are described below.

TORSION PENDULUM. The curved surface of a disk of the material of uniform, known thickness is rendered resistant to gas by the application of a uniform impermeable surface covering. The disk is suspended axially on a quartz fiber in a vessel into which the gas can be introduced at a definite measured pressure. At intervals, the disk is set in oscillatory rotational motion and the oscillation period is determined. If the weights of the disk, of the surface covering and of the gas absorbed are w_D , w_C , and w_G , respectively, and if the times to describe a certain number of oscillations for the unprotected disk, for the protected disk, and for the protected disk containing absorbed gas are T_D , T_{DC} , and T_{DCG} , respectively:

$$w_G = \frac{T_{DCG}^2 - T_{DC}^2}{T_D^2} \times w_D$$

Alternately, the determination of the oscillation period of the uncovered disk may be omitted, and

$$w_G = \left[\frac{T_{DCG}^2}{T_{DC}^2} - 1 \right] (w_D + 2w_C)$$

The shape and covering of the test-piece allow Equation 12 to be applied to determine the diffusion constant.

The apparatus shown (Figure 5), which was constructed of glass, was used to follow the absorption of sulfur dioxide by various substances at atmospheric pressure. After the initial measurements had been carried out in air (the solubility of which is negligibly small compared with that of sulfur dioxide), sulfur dioxide was passed through the apparatus at a constant rate and the oscillation period measured from time to time. (When sulfur dioxide is used, it is necessary to exclude sunlight in order to prevent photochemical action.) With gases such as nitrogen, which are much less soluble than sulfur dioxide, higher pressures must be employed, in order that the absorbed gas may bring about readily measured alterations in the oscillation periods. A metal pressure vessel with thick glass

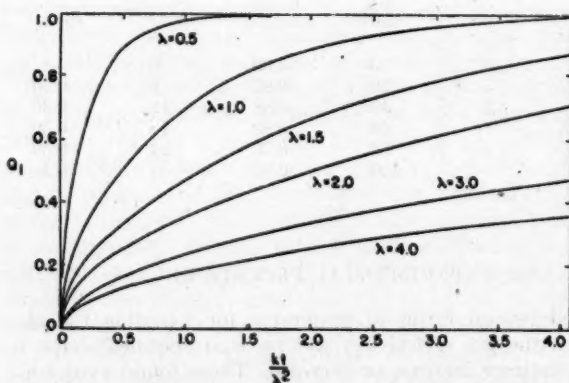


FIG. 4.—Variation of fractional quantity of gas absorbed by sheets of different thicknesses with time.

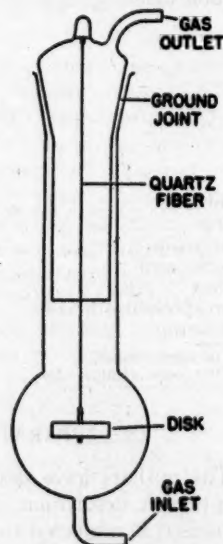


FIG. 5.—Apparatus for gas absorption by disk.

windows, capable of withstanding a pressure of 150 atmospheres, has been used for this purpose.

A possible objection to this method is that the absorption of gas may result in swelling of the disk and consequent alteration of the radius of gyration. The objection can be overcome by measuring, for example, the absorption of gas by two identical cubes, having appropriate surface coverings if desired, fixed symmetrically on a light rod suspended horizontally on a quartz fiber, the distance between the cubes being several times as great as their linear dimensions (Figure 6), or by other modifications of the same principle.

The torsion pendulum has also been used to show that the solubility of gases in rubberlike materials is in accordance with Henry's law.

The material, in the form of thin thread, is helically wound on a light cylindrical frame suspended axially on a quartz fiber, and the whole is enclosed in a suitable gas-tight vessel. (The cylinder and thread are previously weighed, and the oscillation periods of the cylinder alone, and the cylinder and thread, are de-

terminated.) The gas at a definite pressure is introduced into the vessel, and when equilibrium is attained the oscillation period is noted. The obvious calculation gives the amount of gas absorbed at saturation at the particular gas pressure. The use of thin thread, helically wound to expose maximum surface, ensures rapid attainment of equilibrium.

Figure 7, which records experiments carried out with rubber thread and sulfur dioxide, shows that the solubility is proportional to the pressure.

VOLUME MEASUREMENTS AT CONSTANT PRESSURE. One form of the apparatus suitable for use with gases of solubilities comparable with that of nitrogen is shown in Figure 8.

The specimen, in the form of a long square-sectioned rod, is sealed into the narrow tube in the manner shown, the dimensions being so chosen that the free space in the tube containing the specimen is small. When the apparatus is placed in the vertical position (tap downwards), the mercury is out of contact with the

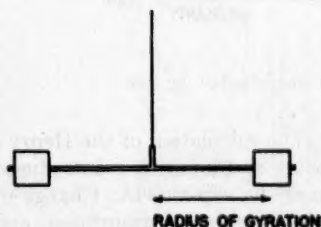


FIG. 6.—Torsion pendulum.

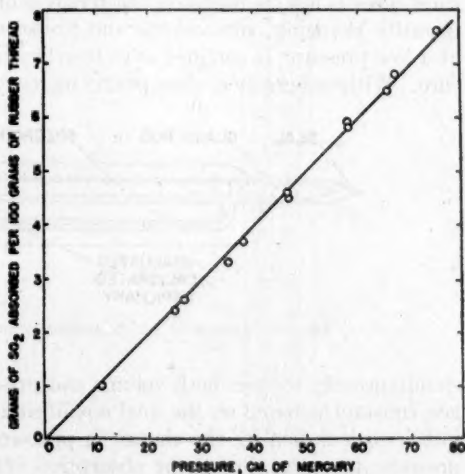


FIG. 7.—Variation of solubility of sulfur dioxide in rubber thread with variation of gas pressure.

capillary and there is free gaseous connection between this and the main tube. With the apparatus in this position the initial gas pressure is produced inside, by introducing or withdrawing gas through the tap, and this pressure is maintained constant until equilibrium is reached. The pressure is then increased to its new value and the tube turned until the capillary is horizontal and in contact with the mercury. As gas is absorbed the mercury moves along the capillary and the volume absorbed at any time (measured at the pressure of the experiment) is equal to the bore of the capillary multiplied by the distance of movement of the mercury meniscus. The quantity of gas absorbed is negligibly small compared with the total quantity in the apparatus and so the fall in pressure during the experiment is also negligibly small.

The dimensions of the bulb and the quantity of mercury in it are so arranged that the height of the free surface of the mercury above the axis of the capillary is equal to the extent to which mercury would be depressed by virtue of its surface tension in a vertical tube of the same dimensions as the capillary tube. There is thus no pressure, positive or negative, on the gas in the specimen-containing tube due to the mercury, and the meniscus is free to move as gas is absorbed.

Equation 12 or 13 may be applied to determine the diffusion constant according, respectively, as the specimen has been covered on two opposite faces or left uncovered. For the calculation of the Henry's law constant, the free space in the specimen-containing tube must be determined. This type of apparatus works well at pressures of several atmospheres, but is less satisfactory at lower pressures.

PRESSURE MEASUREMENTS AT CONSTANT VOLUME. Experiments have been carried out in which the desorption of gas from a specimen in a vacuum, after saturation at a definite pressure of 1 to 2 atmospheres, is followed by measuring pressure change at constant volume due to the desorbed gas. The apparatus, although giving satisfactory results, is comparatively inconvenient and is not described here.

MEASUREMENTS INVOLVING SIMULTANEOUS CHANGE IN VOLUME AND PRESSURE. An experimental method which is very conveniently applied in the important cases of gases such as nitrogen and hydrogen, where the solubility in rubber-like substances is low, is based on the removal of gas by absorption from a reference quantity changing both volume and pressure. The specimen, saturated with gas at a low pressure, is confined over mercury in a quantity of gas at a higher pressure. With progressive absorption, mercury rises into the enclosed space and

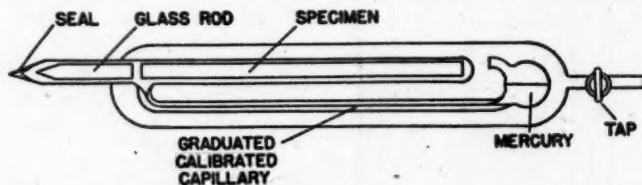


FIG. 8.—Apparatus for measuring volume of gas absorbed by rod.

simultaneously reduces both volume and pressure. The calculation of the Henry's law constant is based on the final equilibrium pressure and no error is introduced into its calculation by the change in pressure during the experiment. Change of pressure, however, during the absorption affects the progress of absorption, and for a strict calculation of the diffusion constant, the experimental results cannot be used in Equations 12, 13, and 14. It is shown below, however, that, if the change in pressure is not great, the error is small.

A simple form of the apparatus is shown in Figure 9.

The specimen of square cross-section is sealed inside a glass tube, one end of which is fused to a communicating graduated capillary tube of known bore. The dimensions are so chosen that the internal free space is small. To prevent possible harm to the specimen during sealing of the tube, it may be convenient to insert a short, well-fitting glass rod (as shown) behind the specimen. The loaded tube is suspended from the stopper of the large outer vessel by means of a wire sealed into a small piece of sealing wax, so that when the stopper is secured in place with a gas-tight fit, the capillary tube does not reach the mercury contained in the outer vessel.

The initial gas pressure is produced in the assembled apparatus, using the tap, and is maintained until equilibrium is reached. The pressure is then increased to the new value, the tap is closed, and the sealing wax support is softened by a small flame applied externally, to allow the capillary to descend into the mercury. The pressure inside the specimen-containing tube is originally the same as

that in the outer vessel, but as gas is absorbed by the specimen the pressure falls and mercury ascends the capillary. The position of the mercury meniscus is noted from time to time. The total quantity of gas in the whole apparatus is great compared with the quantity absorbed, so that the alteration in pressure in the outer vessel due to the absorption is negligible. At equilibrium the final saturation pressure is that of the gas in the outer vessel, less the back pressure due to mercury in the capillary. At the conclusion of the experiment, the free volume of the tube containing the specimen is determined by weighing before and after

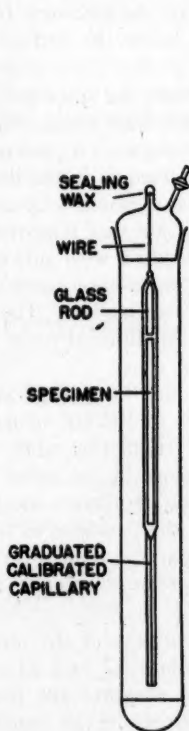


FIG. 9.—Apparatus for measuring gas absorption by rod.

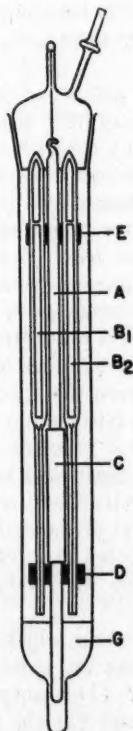


FIG. 10.—Apparatus for testing six specimens.

filling with water. This volume is required, together with the initial and final equilibrium pressures, to calculate the Henry's law constant.

The pressure measurements made during the course of the experiment may be used directly, with little error, to calculate the diffusion constant from Equation 12 or 13 according, respectively, as the specimen has been covered on two opposite faces or left uncovered.

The preferred form of the apparatus, which was designed to test six specimens simultaneously, is shown in Figure 10.

Around a central rod, A , suspended from the stopper by means of a wire and sealing wax, are arranged six tubes, B_1 to B_6 , containing the specimens (only two tubes are shown in the diagram). The specimens are in the form of rods 15 cm.

long and 0.4 by 0.4 cm. in cross-section. Behind the capillary tubes is a cylindrical paper scale, *C*. The tubes and scale are held in position on the rod by means of the cork, *D*, and the binding, *E* (ordinary adhesive tape). The coarsely ground stopper is secured in a gas-tight fit in the main vessel by means of sealing wax. (This method of securing the stopper is capable of satisfactorily withstanding an internal excess pressure of several atmospheres at 30° C. A thin layer of warm sealing wax is applied to the ground surfaces, previously warmed to about 100° C., and the stopper is firmly pressed into position in its seating, expelling most of the sealing wax. The apparatus is allowed to cool.) The ends of the capillaries are arranged to be about 0.5 cm. above the surface of the mercury, *G*, when the central rod is suspended, and they dip about 1 cm. below the surface when it is lowered.

In a large number of experiments with this apparatus, the specimens, originally containing very little gas (the whole apparatus having been evacuated to a pressure of about 2 cm. of mercury), were confined in nitrogen at a pressure of about 200 cm. of mercury and 30° C. The apparatus, assembled as in the diagram, was placed in a thermostat at 30° C. and was maintained evacuated by means of an ordinary water pump, until nearly all the dissolved air was removed from the specimens (at least 24 hours). The apparatus was filled with nitrogen at one atmosphere pressure and reevacuated. This procedure was necessary because the removal of foreign gases by a single evacuation was inadequate. The apparatus was maintained evacuated for at least 48 hours for equilibrium to be reached at this low initial pressure of nitrogen.

To commence the experiment, nitrogen at 30° C. was introduced into the apparatus at a fairly rapid, steady rate until a pressure of 195 cm. of mercury was reached. This pressure was maintained while the capillaries were allowed to descend (as described) into the mercury. The pressure in the outer vessel was then further increased until the mercury rose in the capillaries to the level of the lower part of the scale. The tap was closed and the positions of the mercury levels were noted at intervals. The filling of the apparatus took several minutes, and zero time was taken at the point when the pressure reached 130 cm. of mercury.

The small error which is introduced into the calculation of the diffusion constant by using the scale readings directly in Equations 12 and 13 arises from two sources: (1) absorption does not take place at constant gas pressure (see Figure 11) and (2) the movement of the mercury level in the capillary is not directly proportional to the quantity of gas removed by absorption. It can be shown that the maximum possible fractional error, introduced into the readings and arising from the first source by the assumption that the absorption takes place at a constant pressure equal to the final equilibrium pressure, is

$$\frac{P_1 - P_2}{P_1 - P_0}$$

where

P_0 = initial equilibrium pressure

P_1 = pressure under which absorption takes place at the commencement of the experiment

P_2 = final equilibrium pressure

It is seen from Figure 11 that the average probable error, however, is much lower than this maximum and may be roughly approximated by

$$\frac{1}{2} \times \frac{P_1 - P_2}{P_1 - P_0}$$

The fractional error arising from the second source can be shown to be

$$\frac{bx}{P_1b + V - bx}$$

where

b = bore of the capillary

x = movement of the mercury level in the capillary

V = initial free volume in the tube containing the specimen

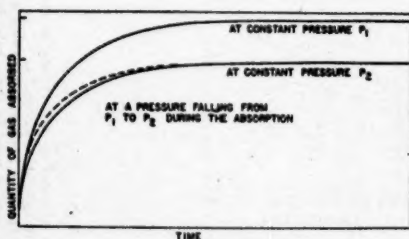


FIG. 11.—Absorption of gas.

Broken line applies to pressure falling from P_1 to P_2 during the absorption.

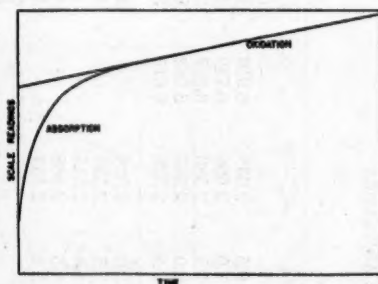


FIG. 12.—Absorption and oxidation.

The following values, taken from a typical experiment on the absorption of nitrogen by soft rubber, may be quoted to assess the order of the error:

$$\begin{aligned} P_0 &= 1.8 \text{ cm. of mercury} \\ P_1 &= 204.6 \text{ cm. of mercury} \\ P_2 &= 199.0 \text{ cm. of mercury} \\ b &= 5.03 \times 10^{-3} \text{ cc. per cm.} \\ V &= 2.87 \text{ cc.} \end{aligned}$$

The total movement of the mercury level in the capillary, $P_1 - P_2$, was 5.6 cm. We assess the error halfway through the absorption, that is, when $x = 2.8$ cm. It is found that

$$\frac{1}{2} \times \frac{P_1 - P_2}{P_1 - P_0} = 1.38 \times 10^{-2}$$

and

$$\frac{bx}{P_1b + V - bx} = 0.36 \times 10^{-2}$$

The total fractional error in the scale readings is therefore 1.74×10^{-2} , which corresponds with an error of about 2 to 3 per cent in the deduced value of the diffusion constant. The small degree of this inaccuracy justifies the use of this very convenient form of apparatus.

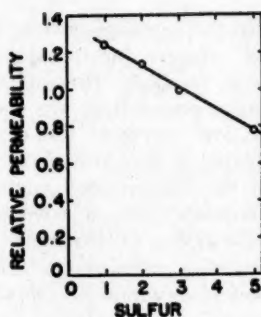


FIG. 13.—Degree of vulcanization of rubber (Table IV, A).

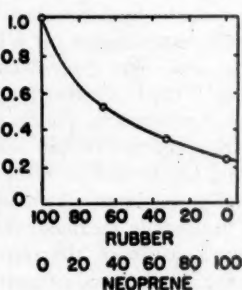


FIG. 14.—Mixtures of rubber and neoprene (Table IV, B).

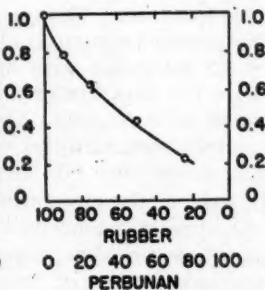


FIG. 15.—Mixtures of rubber and perbunan (Table IV, C).

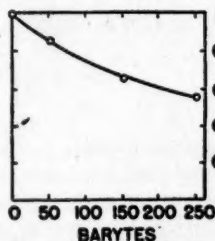


FIG. 16.—Rubber compounded with mineral barytes (Table IV, D).

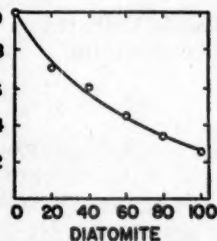


FIG. 17.—Rubber compounded with diatomite (Table IV, E).

The Henry's law constant can be calculated without error. If

P_0 = initial equilibrium pressure, cm. of mercury

P = pressure in outer vessel at commencement of experiment, cm. of mercury

r_0 = initial scale reading, cm.

r_∞ = final scale reading, cm.

r_z = height of scale zero above level of mercury in outer vessel, cm.

b = bore of capillary, cc. per cm.

V = initial internal volume of tube containing specimen

t = temperature, °C.

and

V_s = volume of specimen, cc.

$$h = \frac{1}{76} (r_\infty - r_0) [V + b(P - r_\infty - r_z)] \times \frac{1}{(P - P_0 - r_\infty - r_z)} \times \frac{1}{V_s} \times \frac{273}{(273 + t)} \quad (15)$$

This value for h may be regarded as the change of concentration, measured in cubic centimeters of gas at normal temperature and pressure, per cubic centimeter of absorbent, for a change of gas pressure of 1 cm. of mercury at the temperature of the experiment.

In many of the experiments which were carried out with nitrogen, the nitrogen used was the commercial gas produced by the fractional distillation of liquid air.

This contains about 2 per cent of oxygen and during the experiments this was sufficient to bring about an appreciable steady fall of pressure due to oxidation of the specimens. Thus no definite final pressure was reached. The difficulty was overcome by continuing the experiments for a longer period than was necessary for saturation with nitrogen. The later "oxidation" parts of the curves (Figure 12) were straight lines³, which when extrapolated to zero time gave the required scale readings. The experimental points of the "absorption" parts of the curves were corrected for oxidation on the assumption that oxidation proceeded at the same rate during the period of rapid absorption of nitrogen³.

In some of the experimental procedures which have been outlined, the design of the apparatus renders it impossible to make direct observation of the scale readings at zero time, mainly because of the impossibility of applying an instantaneous isothermal increase in the gas pressure. These zero readings can, however, be calculated from the readings taken during the absorption and from the shape of the absorption curves (Equations 11, 12, and 13).

When the shape of the specimen is such that diffusion of dissolved gas takes place in one direction only, the absorption curve is a parabola up to a fractional saturation of about 0.60. Hence, if attention is confined to this initial part of the curve, it can be shown that

$$r_0 = r_2 - 2r_1$$

where

r_0 = scale reading at zero time

r_1 = scale reading at time t_1

r_2 = scale reading at time t_2

and where t_1 and t_2 are arbitrarily chosen so that $t_2 = 4t_1$

It is desirable to use several such corresponding values of t_1 and t_2 and to average the values of r_0 to obtain a trustworthy value for use in the subsequent calculations.

When the shape of the specimen is such that diffusion of dissolved gas takes place in more than one direction, use may be made of the relationships:

$$1 - Q_2 = (1 - Q_1)^2$$

and

$$1 - Q_3 = (1 - Q_1)^3$$

deduced from Equations 12, 13, and 14, to show that (again confining attention to the initial parts of the curves):

$$r_\infty - r_0 = [2\sqrt{r_\infty - r_2} - \sqrt{r_\infty - r_1}]^2$$

and

$$r_\infty - r_0 = [2\sqrt[3]{r_\infty - r_2} - \sqrt[3]{r_\infty - r_1}]^3$$

for two-directional diffusion (up to a fractional saturation of 0.84), and for three-directional diffusion (up to a fractional saturation of 0.96), respectively. The value of r_∞ is already known, and hence r_0 can be determined.

EXPERIMENTAL RESULTS

A typical calculation from a set of observations obtained with the apparatus shown in Figure 10, using as specimen a square-sectioned rod of soft rubber, covered only on its square faces, and commercial nitrogen, is given in Table III.

The specimen was made from the rubber mix:

Rubber	100
Sulfur	3
Zinc oxide	5
Stearic acid	2
Nonox	1
Mercaptobenzothiazole	1

vulcanized in the form of a square rod $0.4 \times 0.4 \times 14.6$ cm. by heating for 60 minutes at 150° C. The square ends only were covered with tinfoil, applied by means of a suitable adhesive.

The other experimental details were:

$P_0 = 2.2$ cm. of mercury

$P = 205.7$ cm. of mercury (barometric pressure, 76.2; excess pressure, 129.5)

$r_0 = 2.40$ cm. (scale divisions were centimeters)

$r_\infty = 9.14$ cm. (scale divisions were centimeters)

$r_s = 3.00$ cm. (scale divisions were centimeters)

$V = 2.80$ cc.

$b = 6.23 \times 10^{-3}$ sq. cm.

$V_s = 2.34$ cc.

$a = 0.40$ cm.

$t = 30.0 \pm 0.1^\circ$ C,

These values, inserted in Equation 15, give $h = 7.15 \times 10^{-4}$, where concentration is measured in cubic centimeters of gas at normal temperature and pressure per cubic centimeter, and gas pressure is measured in centimeters of mercury.

The average value of σ is used to calculate the diffusion constant from the relationship $k = \frac{\sigma}{\rho} \left(\frac{a}{\pi} \right)^2$ sq. cm. per second, where $\rho = 0.514$. Substituting these

values, $k = \frac{4.63 \times 10^{-5}}{0.514} \times \left(\frac{0.4}{\pi} \right)^2$ sq. cm. per second $= 1.46 \times 10^{-6}$ sq. cm. per second.

Correction may be made for small variations in the dimensions of the test-pieces by substituting for the value of a^2 the true cross-sectional area. For example, if the cross-sectional dimensions of the test-piece had been 0.395 and 0.403 cm., the value 0.395×0.403 would have been used in place of $(0.4)^2$.

The product kh , $1.46 \times 10^{-6} \times 7.15 \times 10^{-4} = 1.03 \times 10^{-9}$, is directly proportional to the permeability of a standard sheet under standard conditions. For a comparison of the permeability of the material of this test-piece to nitrogen with that of a second material, this value is referred directly to the corresponding value for the second material. If it is desired to interpret the result directly in terms of permeability, the values of kh and of the chosen conditions may be inserted in Equation 3:

$$Q = -kA \frac{h(p_2 - p_1)}{L} t$$

If $A = 100$ sq. cm., $L = 0.1$ cm., $(p_2 - p_1) = 76$ cm. of mercury, and $t = 1$ hour, then $Q = -0.29$ cc. at normal temperature and pressure. The negative sign indicates that the gas passes from the high- to the low-pressure side.

Table IV and Figures 13 to 17 give further experimental results obtained with the same apparatus under similar conditions.

In these experiments, the gas used was commercial nitrogen, the temperature was 30° C., and the test-pieces were uncovered square rods $0.4 \times 0.4 \times 15.0$ cm.

TABLE IV

EXPERIMENTAL RESULTS

A. DEGREE OF VULCANIZATION OF RUBBER

Rubber		Sulfur	k	h	kh
Rubber	100				
Zinc oxide	5	1	1.24	1.00	1.24
Stearic acid	2	2	1.09	1.04	1.14
Nonox	1	3	1.00	1.00	1.00
Mercaptobenzothiazole	1	5	0.81	0.98	0.79

B. MIXTURES OF RUBBER AND NEOPRENE^a

Rubber + Neoprene		Rubber	Neoprene	k	h	kh
Rubber + Neoprene	100					
Sulfur	3	100	0	1.00	1.00	1.00
Zinc oxide	5	67	33	0.58	0.89	0.52
Light magnesium carbonate	5	33	67	0.40	0.86	0.34
Stearic acid	2	0	100	0.26	0.89	0.23
Nonox	1					
Mercaptobenzothiazole	1					

C. MIXTURES OF RUBBER AND PERBUNAN

Rubber + Perbunan		Rubber	Perbunan	k	h	kh
Rubber + Perbunan	100					
Sulfur	3	100	0	1.00	1.00	1.00
Zinc oxide	5	90	10	0.83	0.95	0.79
Stearic acid	2	75	25	0.70	0.91	0.63
Nonox	1	50	50	0.54	0.80	0.43
Mercaptobenzothiazole	1	25	75	0.32	0.69	0.22

D. RUBBER COMPOUNDED WITH MINERAL BARYTES

Rubber		Barytes	k	h	kh
Rubber	100				
Sulfur	3	0	1.00	1.00	1.00
Zinc oxide	5	50	0.91	0.94	0.86
Stearic acid	2	150	0.81	0.82	0.66
Nonox	1	250	0.80	0.70	0.56
Mercaptobenzothiazole	1				

E. RUBBER COMPOUNDED WITH DIATOMITE

Rubber		Diatomite	k	h	kh
Rubber	100				
Sulfur	3	0	1.00	1.00	1.00
Zinc oxide	5	20	0.83	0.85	0.71
Stearic acid	2	40	0.81	0.74	0.60
Nonox	1	60	0.71	0.63	0.45
Mercaptobenzothiazole	1	80	0.64	0.54	0.34
		100	0.57	0.46	0.26

F. KOROSEAL^b

Rubber			k	h	kh
Rubber	100				
Sulfur	3				
Zinc oxide	5				
Stearic acid	2		1.00	1.00	1.00
Nonox	1				
Mercaptobenzothiazole	1				
Koroseal	—		0.16	0.42	0.07

^a Commercial grade G.^b Goodrich plasticized polyvinyl chloride.

In the mixes the proportions are given as parts by weight. Vulcanization was 1 hour at 150° C. The results are given as relative values.

SUMMARY AND CONCLUSIONS

The rate at which a gas passes through a sheet of rubber-like material and the rate at which a gas is absorbed by a block of the material both depend on the same factors, solubility and diffusion constant. The magnitude of these factors can be measured by absorption experiments carried out under specified conditions and the results can be used to assess the permeability of the material in sheet form. Experimental methods and suitable apparatus are described for following absorption and the manner of interpreting the results in terms of permeability is given. Besides such advantages as accurate temperature control, convenient size and ease of handling of the apparatus, the small size of the test-piece, and the elimination of the difficulty of producing uniform thin sheets free from pinholes, the method has the advantage that both factors, solubility and diffusion constant, can be assessed independently; this is not normally possible with direct permeation measurements. Some experimental results are tabulated.

ACKNOWLEDGMENT

Grateful acknowledgment is made to the Dunlop Rubber Co., Ltd., for permission to publish this investigation.

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TENSILE PROPERTIES OF RUBBER COMPOUNDS AT HIGH RATES OF STRETCH *

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I. INTRODUCTION

It has been suggested by several authors that some relationship may exist between the stress-strain properties of a rubber compound and its resistance to abrasive wear. Wiegand¹ pointed out in 1920 that since the wear of a tire tread consists in the gouging or tearing out of small masses of rubber, the resistance to abrasive wear might depend on the amount of work performed in stretching the rubber to rupture. A chart accompanying this suggestion showed that, for a compound containing 25 volumes of channel black per 100 volumes of rubber, this work was greater than for compounds containing other fillers or other proportions of channel black. It is well known that compounds containing from 25 to 35 volumes of channel black have the highest resistance to abrasive wear. Greider² found no exact proportionality between the work of extension and abrasive resistance obtained in the laboratory, but compounds which showed high resistance to abrasion also showed relatively large work of extension. In a more recent investigation on the reinforcement of rubber with carbon black, Wiegand³ states that the resistance of a rubber compound to abrasive wear is undoubtedly influenced not only by the work of extension to rupture but also by the work of extension to intermediate elongations.

Principally because of experimental difficulties in obtaining simultaneous values of extension and force at high rates of stretch, most of the previous investigations have been limited to relatively slow rates. However, it has long been known that the tensile properties of a vulcanized rubber compound depend on the rate at which the specimens are stretched. In 1903 Bouasse and Carrière⁴ noted that for a rubber-sulfur compound the extension of a specimen for a given load was greater when the load was applied slowly than when it was applied quickly. The extensions were carried out to about 600 per cent of the unstretched length of the specimens at rates ranging from 0.5 to 7 per cent per second⁵. Somerville, Ball and Edland⁶ noted for a more modern pure-gum compound a similar effect of stretching rates from 0.3 to 3 per cent per second and for extensions to 350 per cent.

Holt⁷, using an autographic machine, stretched a tire-tread compound to an elongation of 450 per cent at average rates ranging from 10 to 1,500 per cent per second. His results also show that for any given strain the stress increases with increasing rate of stretch. Similar results were obtained by Dart and Guth⁸, who used a method involving photographic recording and employed rates ranging from 2 to 300 per cent per second.

The effects of average rates of extension from about 2 to 20 per cent per second on the tensile strengths and ultimate elongations for four compounds were reported by the National Bureau of Standards⁹ in 1915. The study showed

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slightly higher tensile strengths and ultimate elongations for the higher rates of stretch.

The above-mentioned investigators have found small increases in the stress for a given strain, but no one reported any marked advantage in making tests at the higher rates of stretch. Beadle and Stevens¹⁰ suggested the use of the impact pendulum for stretching rubber test specimens in order that the tests be made to approach more nearly the sudden stresses experienced by a tire on the road. Later studies by investigators^{11, 12}, using the impact pendulum to determine the work done in stretching rubber to rupture, report that high rates of stretch are advantageous in determining the best cure. Stress-strain curves obtained for elongations up to 350 per cent at a rate of about 8,000 per cent per second by means of a modified impact pendulum¹² show stress which are relatively large compared with those obtained by the usual methods of testing.

In a recent investigation of isothermal and adiabatic stress-strain curves for pure-gum compounds, Hauk and Neumann¹³ found that for compounds containing 1 and 2 per cent of sulfur "the curves first separate, then at higher elongations approach each other, and finally intersect." In this work the isothermal curves were determined by loading similar strip-specimens with various weights and observing the change in distance between gage marks. The adiabatic curves were determined by applying the stretching force through a calibrated spring and obtaining a cinematographic record of the relative positions of gage marks on both the specimen and the spring. The stretching process for the adiabatic curves was accomplished in less than a second. The same authors¹⁴, working with elongations up to about 450 per cent, found in another investigation that for various rates of stretch ranging from 50 to 700 per cent per second the stress increasing with increasing rates.

The purpose of the present investigation was to determine whether the tensile properties measured at high stretching rates offer any better indication of resistance to abrasive wear than the properties measured at the usual testing rates. In this study stress-strain relationships were determined for different types of rubber compounds when stretched rapidly to rupture. The specimens were stretched to rupture in less than a second, so that the tests were nearly adiabatic. The cross-sections of the specimens were small compared to their lengths, so that the stresses might approach simple tensions in character. To make the results for high rates of stretch comparable to those for low rates, similar specimens were used throughout the study.

II. RUBBER COMPOUNDS INVESTIGATED

Tests were made on a series of specimens of each of four rubber compounds, the compositions and cures of which are shown in Table I. The first compound is referred to as "pure gum", that is, it contains no filler. The compounds containing fillers, have a base stock which is as nearly like the pure-gum compound as is practicable. Each compound contains 25 volumes of filler per 100 volumes of crude rubber.

In the selection of the compounds to be studied, the aim was to pick a few simple compounds containing commonly used fillers and differing considerably in tensile and abrasive properties. The addition of channel black to a base stock produces a compound which possesses the greatest resistance to abrasive wear, and which is universally used for tire treads. The compound is stiff and has markedly higher tensile strength than the base stock. When clay is added to

the base stock, a stiff compound with relatively low tensile strength and ultimate elongation results. Soft black, however, has little stiffening action, and a soft-black compound has a relatively high ultimate elongation. Such a compound has a tensile strength less than that of the channel-black compound but more than that of the clay compound.

TABLE I
COMPOSITION AND CURE OF RUBBER COMPOUNDS

Rubber compounds	Pure gum	Channel black	Soft black	Clay
Ingredients*	Parts by weight			
Rubber (smoked sheet).....	100	100	100	100
Sulfur	3	3	3	3
Zinc oxide	5	5	5	5
Stearic acid	1	2	2	2
Benzothiazyl disulfide (Altax).....	1.0	1.0	1.0	1.0
Tetramethylthiuram disulfide (Tuads)....	—	0.1	0.1	0.1
Phenyl-beta-naphthylamine	1.5	1.5	1.5	1.5
Channel black (Micronex).....	—	49.0	—	—
Soft carbon (P-33).....	—	—	49.0	—
Clay (Dixie)	—	—	—	70.7
Curing temperature (° C.).....	142	127	127	127
	20	20	10	20
	25	25	*15	25
	*30	*35	20	*35
Curing time (min.).....	40	50	25	50
	60	75	35	75
	75	—	—	—

* Cures selected as optimum for comparison in the present investigation.

III. APPARATUS AND PROCEDURE

The tensile properties for high rates of stretch were determined by means of a special apparatus in which ring specimens were stretched by means of a falling weight. Slow stretching rates were obtained by use of a modified form of this apparatus and by a Scott tensile machine.

1. RAPID STRETCHING

(A) DESCRIPTION OF APPARATUS

A schematic diagram of the apparatus employed in obtaining stress-strain relationships for high rates of elongation is shown in Figure 1. Ring specimens are stretched to rupture by a falling weight, and their stress-strain relationships are determined from a study of the position of the weight as a function of time. The position of the weight is recorded at equal time intervals on a paper tape, one end of which is fixed to the weight. The tape is pulled through a spark gap as the weight falls. The timing of the sparks is controlled by a tuning fork which operates the breaker points in the primary circuit of an induction coil. The frequency of the tuning fork is 55.6 vibrations per second, and the time required to stretch a specimen to the point of rupture ranges from about one-half to three-quarters of a second. The time involved in stretching the specimen is short enough so that the test may be considered nearly adiabatic. The rate of

stretch is not constant, but the average is in the order of 1,000 per cent per second. The maximum speeds range from 1,600 to 1,950 per cent per second for the pure-gum compounds and from 950 to 1,500 per cent per second

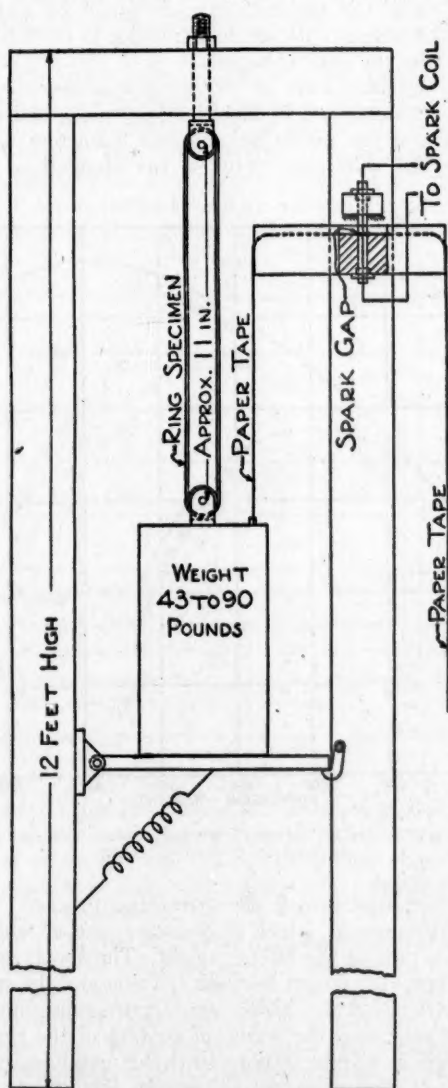


FIG. 1.—Schematic diagram of the apparatus for determining the tensile properties of rubber by the use of a falling weight.

for the loaded compounds. The actual rates of stretch for a pure-gum and a loaded compound are shown in Figure 2. The fact that the speed for the channel-black specimen selected for this figure does not start from zero indicates that

the weight fell some distance before beginning to stretch the specimen. In the case of the pure-gum specimen selected, this distance was zero, and therefore the speed starts from zero. The channel-black and pure-gum specimens selected here were stretched by weights of 90.2 and 42.93 pounds, respectively. Variations in the rate of stretch of the specimen brought about by changes in the weight or in the distance the weight falls before beginning to stretch the specimen have no observable effect on the data obtained.

The molded-ring specimens are of rectangular cross-section, with inside and outside diameters of about 7 and 7 $\frac{1}{4}$ inches, respectively, and a width of 0.2 inch. The difference between the inside and outside diameters was made relatively small to minimize the difference between the elongations of the inner and

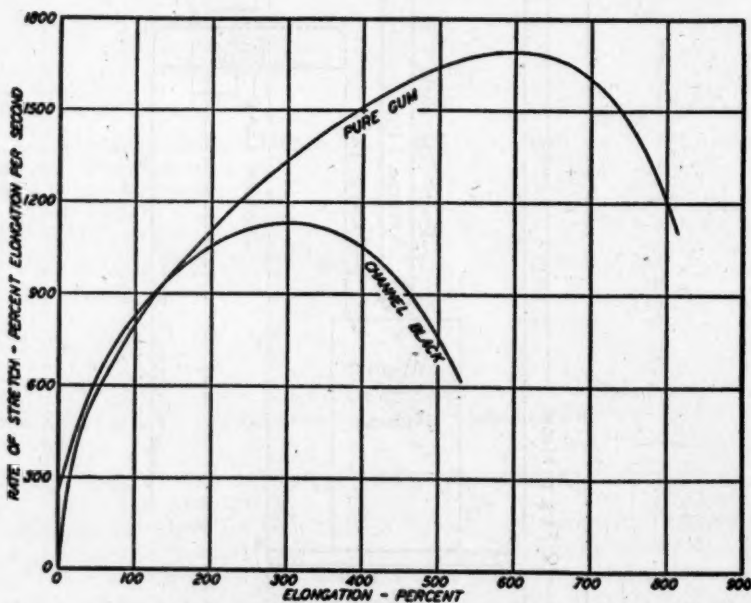


FIG. 2.—Rates of stretch for typical specimens of channel-black and pure-gum compounds when stretched by the falling weight.

outer surfaces of the rings during the stretching process. The specimens are supported on two steel spools, $\frac{3}{8}$ inch in diameter, one of which is fixed in position and the other is part of the falling weight. The spools are free to rotate on their axes, and the areas of contact between the ring and the spools are lubricated with castor oil. Except for the highly cured pure-gum compounds, few specimens rupture in or very near the region of contact of the rings with the spools.

The weight is made in several sections so that it can be varied between 43 and 90 pounds by steps of approximately 12 pounds. The upper or fixed spool may be raised or lowered to allow the weight to fall any desired distance (usually from 0 to 2 inches) before beginning to stretch the specimen.

The spark electrodes consist of tungsten wires inside glass capillary tubes. The bore of these tubes is about 0.020 inch, and the electrode ends of the wires reach to within about 0.010 inch of the ends of the tubes. The recording tape slides between the tubes, and the tubes are kept in contact with it by the weight

of the upper electrode assembly. Strips of adding-machine paper, $1\frac{1}{4}$ inches wide and 10 feet long, are used for the recording tape. A flat spring keeps the tape taut as the weight falls. The friction of the tape produces no appreciable effect on the motion of the weight since, if the weight is allowed to fall without a specimen in place, its acceleration is found to be equal, within an experimental error of about 1 part in 300, to the accepted value of g , the acceleration of a freely falling body.

The positions of the spark holes in the tape are measured by means of a low-power microscope and a millimeter scale. The distance between any two consecutive holes, after the starting point, is numerically equal to the average speed of the weight during the corresponding time interval and is equal at a first-order approximation, to the instantaneous speed at a time midway between the beginning and end of the interval. Figure 3 shows a typical speed-time graph plotted by this method. Region A corresponds to the free fall of the weight

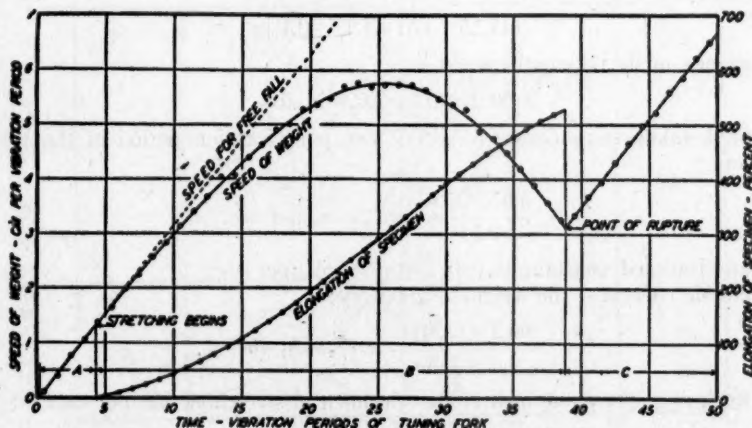


FIG. 3.—Speed-time and elongation-time curves for a specimen of channel black compound stretched by the falling weight.

before it begins to stretch the specimen. The distance of free fall was found by direct measurement before the weight was released, and in this case was 1.1 inches (2.8 cm.). Region B represents the fall of the weight under the action of the upward pull of the specimen. Region C represents the free fall of the weight following the rupture of the specimen.

The tensile properties of the specimen may be determined in either of two ways: (1) the tension in the specimen may be determined at any point during its stretch from the speed-time curve; or (2) the work done by the weight on the specimen may be determined and plotted as a function of its elongation, and the tensile properties may be determined from the resulting graph. In the first method the tension, especially for low elongations, must be obtained from the difference of two relatively large quantities. Consequently, this method was abandoned in favor the less direct method, *viz.*, that of considering the work done by the weight on the specimen.

Since data obtained by allowing the weight to fall without a specimen in place show that frictional forces due to the tape are negligible, the work done on the specimen is equal to the difference between the change in potential energy

of the weight due to its change in position and the kinetic energy due to its speed. The curves in Figure 3 are needed only to determine the speed of the weight as a function of the elongation of the specimen and to determine the ultimate elongation of the specimen.

(B) SAMPLE CALCULATION

A sample calculation for the determination of the work done in stretching the specimen represented by Figure 3 is as follows:

Weight	90.2	lbs.
Frequency of the tuning fork.....	55.6	cycles per sec.
Distance weight falls before beginning to stretch the specimen.....	1.1	in.
Half-circumference of the unstretched specimen.....	11.15	in.
Volume of the specimen.....	0.583	cu. in.

For an elongation of 350 per cent, for example, the distance the weight has fallen is:

$$(11.15 \times 3.5) + 1.1 = 40.1 \text{ in.}$$

The change in its potential energy is:

$$90.2 \times 40.1 = 3,620 \text{ in.-lbs.}$$

Its speed, taken from Figure 3, is 5.67 cm. per vibration period of the tuning fork, or:

$$\frac{5.67 \times 55.6}{2.54} = 124 \text{ in. per sec.}$$

The gravitational constant is $980/2.54 = 386$ in. per sec.

The kinetic energy of the weight is given by:

$$\frac{90.2 \times (124)^2}{2 \times 386} = 1,800 \text{ in.-lbs.}$$

The work done per cubic inch of the specimen in stretching 350 per cent is:

$$\frac{3,620 - 1,800}{0.583} = 3,120 \text{ in.-lbs. per cu. in.}$$

Similar calculations may be carried out for as many elongations as may be desired. Figure 4 shows the work done per unit volume of the sample plotted as a function of the elongation. Since for any given elongation the stress is equal to the ratio of the change in work done per unit volume to the corresponding change in strain, the slope at any point of the work curve, Figure 4, is equal to the stress at the corresponding strain. Therefore the stress-strain curve for the specimen can easily be plotted either from an analytical treatment of the work data or by graphical means. Both methods were employed in the present investigation.

(C) PRECISION

The precision of the measurements for high rates of stretch is as good as can be obtained by the usual testing methods. Table II and III show the work of extension at various elongations of pure-gum and channel-black compounds at optimum cure, and are illustrative of the general precision obtained. The coefficient of variation used in these tables is defined as the ratio of the standard deviation to the mean, the standard deviation being the square root of the mean

of the squares of the deviations of the individual observations from their mean. The coefficients of variation observed at rupture are in good agreement with the value 0.05 stated by Holt and McPherson¹⁵ to be that commonly obtained by the usual testing methods.

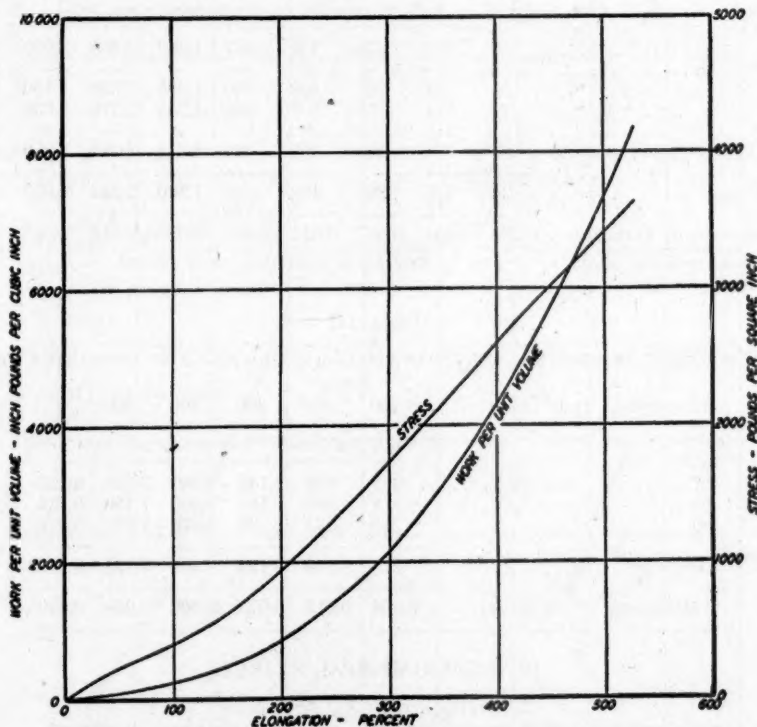


Fig. 4.—Work-elongation curve and the stress-strain curve obtained from it.

The work-elongation curve is derived from figure 3.

2. SLOW STRETCHING

To eliminate the effect of variables other than the rate of stretch, identical specimens were made up for both rates. The stress-strain relationships for slow stretching were determined for all but the pure-gum compounds on a Scott tensile machine, using sections of the rings as strip specimens and toggle clamps¹⁶ to hold the strips. With 2-inch gage marks and a jaw separation of 20 inches per minute, the speed of stretch is 8 to 10 per cent per second. To determine whether the geometry of the specimen or the clamping arrangement affected the observed tensile properties, a number of rings of a carbon-black compound were stretched at about the same rate, 8 to 10 per cent per second, over the lubricated spools used for rapid stretching. The resulting stress-strain curves, including the average ultimate elongations and tensile strengths, were not appreciably different from those obtained with strip specimens of the same compound. Since strips from the pure-gum rings showed a decided tendency to break in or near the clamps, all the data for this compound were obtained by stretching complete rings over the lubricated spools.

TABLE II

WORK OF EXTENSION FOR THE PURE-GUM COMPOUND AT OPTIMUM CURE

Elongation (per cent)...	50	150	250	350	450	550	650	750	{Rup- ture
Work of extension (inch-pounds per cubic inch)									
Ring No.									
257	26	115	274	491	837	1,390	2,265	4,000	5,340
259 ^a									5,510
261	25	124	287	498	840	1,380	2,350	4,130	5,070
262	22	114	279	507	808	1,355	2,270	4,030	5,900
263 ^a									5,520
264	23	120	280	498	828	1,315	2,260	4,080	5,920
Average	24	118	280	498	828	1,360	2,285	4,060	5,543
Coefficient of variation..	0.066	0.034	0.017	0.011	0.015	0.021	0.016	0.012	0.054

^a Values were not calculated for work of extension at elongations below rupture.

TABLE III

WORK OF EXTENSION FOR THE CHANNEL-BLACK COMPOUND AT OPTIMUM CURE

Elongation (per cent).....	100	200	300	400	500	{Rup- ture
Work of extension (inch-pounds per cubic inch)						
Ring No.						
87	216	840	2,140	4,290	7,310	8,330
88	214	859	2,194	4,360	7,456	9,235
89	215	833	2,130	4,270	7,360	9,170
Average	215	844	2,155	4,307	7,375	8,910
Coefficient of variation.....	0.004	0.013	0.013	0.009	0.008	0.046

IV. EXPERIMENTAL RESULTS

1. STRESS-STRAIN RELATIONSHIPS

Stress-strain curves for the optimum cure of each compound are shown in Figure 5. In each case the solid line refers to rapid stretching and the broken line refers to slow stretching. The data corresponding to the points shown are tabulated in Table IV. It will be noted that, for elongations up to about 500 or 600 per cent, the stress at a given elongation is greater for rapid stretching. For the pure-gum compound, the difference in the stresses for the two rates of stretching reaches a maximum of 75 pounds per square inch at 500-per cent elongation. At elongations greater than 600 per cent the difference is negligible. For the loaded compounds the difference is somewhat greater but vanishes at about 500-per cent elongation, and reverses its sign at higher elongations.

The fact that the curves for high rates of stretching approach or cross those for slow stretching is in accord with the observations of Hauk and Neumann¹³. This effect might be accounted for, at least in part, by the greater increase of temperature of the specimen when it is stretched more quickly. This increase of temperature at high stretching rates was greater for the loaded than for the pure-gum compounds. Specimens of the channel-black compound were found, about 15 seconds after rupture, to be at temperatures as much as 25° C. higher than they were before stretching began. A study of the effect of the temperatures of several rubber compounds on their respective tensile stresses, reported by the

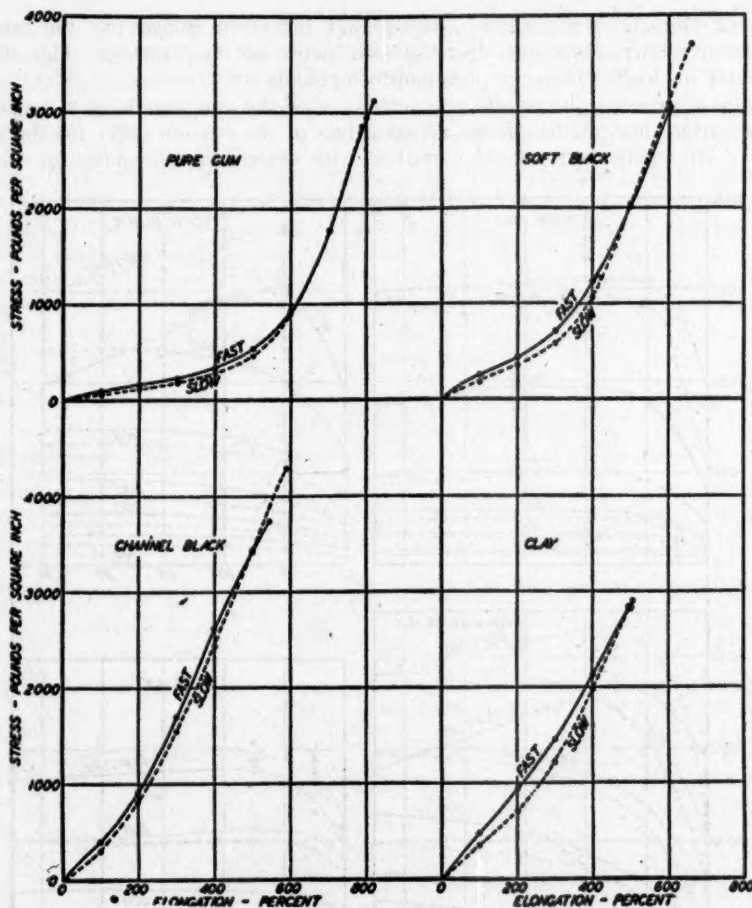


Fig. 5.—Comparative stress-strain curves for two rates of stretch.

The curves are based on the optimum cures of the compounds described in table 1.

TABLE IV

COMPARISON OF STRESSES OF RUBBER COMPOUNDS AT OPTIMUM CURE FOR THE TWO RATES OF STRETCHING

Compound	Pure gum		Soft black		Channel black		Clay	
Rate of stretching.....	Fast	Slow	Fast	Slow	Fast	Slow	Fast	Slow
Elongation (per cent)	Stress (pounds per square inch)							
100	92	56	250	180	390	295	470	345
200	161	107	435	355	910	810	940	705
300	220	173	705	580	1,700	1,540	1,460	1,215
400	329	270	1,225	1,070	2,610	2,430	2,130	1,980
500	530	455	2,010	2,025	3,430	3,415	2,840	2,840
600	912	895	2,990	3,085	—	—	—	—
700	1,770	1,760	—	—	—	—	—	—
Tensile strength	3,120	2,850	3,040	3,705	3,740	4,280	2,840	2,900

National Bureau of Standards¹⁶, shows that for given elongations the tensile stresses of rubber compounds decrease with increasing temperatures. This effect is greater for loaded than for pure gum compounds.

Figure 6 presents the tensile characteristics of the compounds as a function of the curing time. Although the actual values of the stresses differ for the two rates of stretching their general variations with changes in cure differ but little.

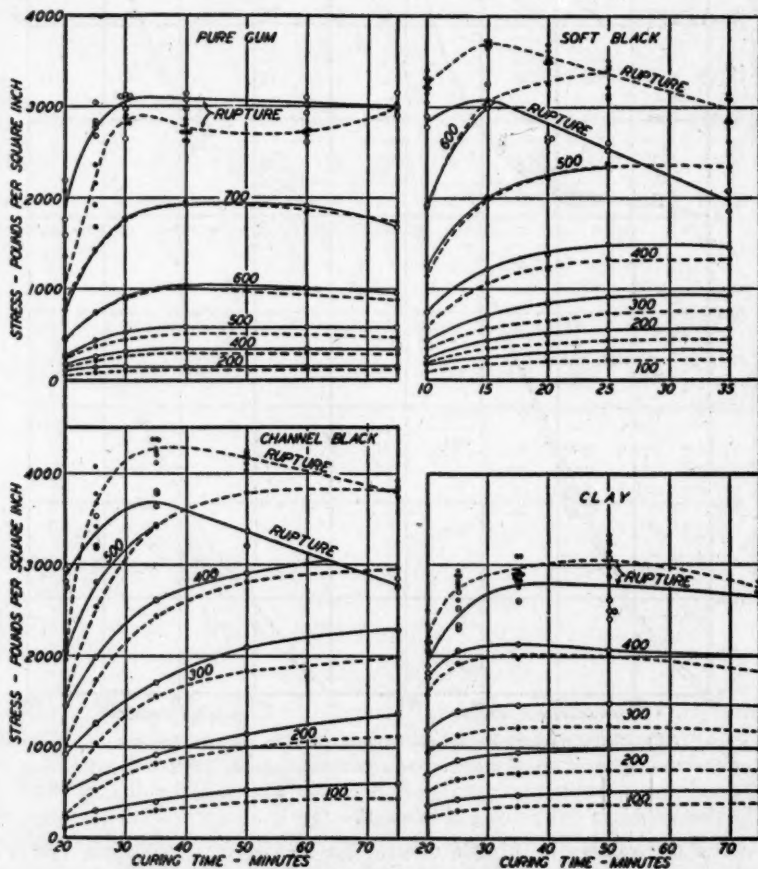


FIG. 6.—Stresses and tensile strengths for the two rates of stretch as a function of the time of cure. The solid-line and broken-line curves refer respectively to rapid and slow stretching. The numbers on the curves indicate the per cent elongation. The compounds are those described in table 1.

In regard to the tensile strengths for the pure-gum compound, it should be mentioned that for cures greater than 30 minutes all the ruptures occurred at or near the supporting spools.

Except for the pure-gum compound and the channel-black compound of lowest cure, the tensile stresses and elongations at rupture are less for rapid than for slow stretching. The differences in the behavior of the loaded and pure-gum compounds at the two rates of stretch are probably due to differences in: (1) the increase of the temperatures referred to above; (2) the behavior of the

specimen at the region of contact with the supporting spools, and (3) the rate and type of fibering¹⁷ of the different compounds. No attempt is made to explain the exact causes of the observed differences.

2. WORK OF EXTENSION

Table V shows the work of extension of the rubber compounds at optimum cure tabulated as a function of elongation. For the compounds investigated, the ratio of the work of extension for slow stretching to that for rapid stretching, at equal elongations, ranges from about 0.6 at 100-per cent elongation to about 0.9 in the neighborhood of rupture. The relative constancy of this ratio at each elongation makes it evident that the work of extension for a given elongation obtained by rapid stretching gives no better indication of the nature of a compound than can be obtained by slow stretching.

TABLE V

COMPARISON OF WORK OF EXTENSION OF RUBBER COMPOUNDS AT OPTIMUM CURE FOR THE TWO RATES OF STRETCH

Compound	Pure gum		Soft black		Channel black		Clay	
	Fast	Slow	Fast	Slow	Fast	Slow	Fast	Slow
Rate of stretching.....	Work of extension (inch-pounds per cubic inch)							
Elongation (per cent)								
100	62	35	140	95	215	135	240	170
200	190	125	465	365	843	670	940	685
300	385	270	1,015	815	2,155	1,820	2,120	1,615
400	645	485	1,960	1,595	4,310	3,785	3,900	3,190
500	1,060	840	3,560	3,095	7,375	6,705	*6,380	5,590
506	—	—	—	—	—	—	—	*5,740
543	—	—	—	—	*8,910	8,270	—	—
590	—	—	—	—	—	*10,200	—	—
600	7,740	1,490	6,060	5,675	—	—	—	—
605	—	—	*6,210	5,835	—	—	—	—
660	—	—	—	*7,735	—	—	—	—
700	3,040	2,770	—	—	—	—	—	—
790	4,990	*4,840	—	—	—	—	—	—
820	*5,540	—	—	—	—	—	—	—

* Values at rupture.

The total work of extension to rupture for the pure-gum and clay compounds is greater for rapid stretching than for slow stretching. On the other hand, for the compounds containing soft black and channel black the work of extension is actually less for rapid stretching. Since the soft-black and channel-black compounds are known to be much more resistant to abrasive wear than the other compounds, it would seem that the work of extension to rupture is less indicative of resistance to abrasive wear when the compound is stretched rapidly than when it is stretched slowly.

V. SUMMARY AND CONCLUSIONS

Stress-strain relationships and the work of extension for four rubber compounds were studied for a rate of stretching of the order of 1,000 per cent per second. This rate is sufficiently great so that the test may be considered to approach adiabatic conditions. A comparison of these data with similar data for a rate of stretching which lies in the range of speeds common to the usual routine tests

shows that increased speed of stretching affects the observed tensile properties as follows: (1) the stresses are increased at elongations up to about 500 per cent for the loaded compounds and up to 600 per cent for the pure-gum compound, the maximum increases ranging from 75 pounds per square inch for the pure-gum compound to 245 pounds per square inch for the clay compound; (2) the stresses in the carbon-black compounds are decreased slightly at elongations near rupture; (3) the work of extension to rupture is increased for the pure-gum and clay compounds and decreased for the carbon-black compounds, and (4) the work of extension for a given elongation is increased for all the compounds. The stresses and the work of extension at the higher speed reveal no information indicative of resistance to abrasive wear that cannot be gained from similar studies of data obtained in stretching the specimen slowly.

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THE HEAT CONDUCTIVITY OF RUBBER *

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A number of papers have been published on the results of investigations of the heat conductivity of rubber^{1, 2, 3, 4, 5}. For most materials, it is sufficient to know the heat conductivity for steady heat currents, a condition which rarely exists in the manufacture and practical use of rubber articles. The technology of rubber deals chiefly with processes which involve the heating and cooling of rubber mixtures, *i. e.*, with variable thermal processes. In this case, the important factor for the manufacturer and technologist is the heat conductivity of a mixture as characterized by the rate of change of temperature inside the mass. The proposed formula⁶ for the distribution of heat along one coördinate x , is:

$$\frac{d\theta}{dt} = a \frac{d^2\theta}{dx^2} \quad (1)$$

where θ is the temperature at a given point, t is the time and $a = \frac{k}{c\gamma}$ *i. e.*, the coefficient of thermal conductivity. Thus, the formula connects the rate of temperature change at a given point with the distribution of heat in the region of this point. A brief examination of the physical significance of the value a shows that the coefficient of heat conductivity k represents the quantity of heat passing in one second through unit area at a temperature gradient equal to one. The product of the specific heat capacity c by the density γ of the material is the volume heat capacity. Hence the relation: $\frac{k}{c\gamma}$, represents the temperature changes in a layer in a unit of time. The meaning of the value a shows that it can be calculated from direct determinations of k , c and γ . However, the determination of the specific heat capacity of rubber is very difficult because of the low heat conductivity. Moreover, the determination of the coefficient of thermal conductivity k requires time-consuming manipulations and the use of special precision devices. Therefore it is more rational to calculate a from Equation (1) by determining experimentally the first product of the temperature in time and its second product on the coördinate. This method was previously used by one of us⁷, although it gives sufficiently accurate results only with thick (not less than 5 cm.) flat-parallel layers of large areas (with samples of small areas a distortion appears as a result of the loss of heat from the edges). In attempts to develop a simple and rapid method for determining the heat conductivity of rubber, which would eliminate the distorting action of the thermal losses at the edges of a sample, it appeared that the use of samples of spherical form would be the most rational procedure. However, the placing of several thermocouples at a definite distance from each other, which is required for the determination of the second product of temperature on the coördinate (radius), is very difficult of execution. Therefore a method was used for the evaluation of thermal conductivity of a sphere from the course of the temperature change in

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its center with a constant temperature of the surrounding medium. The method is based on the theory of cooling or heating of simple bodies, which has already been described^{8, 9}.

PRINCIPLES OF THE METHOD

Let us assume that a sphere of radius R , previously heated or cooled uniformly to temperature θ_0 , is quickly placed in medium c at some other temperature θ_1 . The mathematical interpretation of the process of cooling or heating of a body, including a sphere, is extremely complicated. The calculation can be simplified in such a case when the temperature of a given point of the body is estimated, not from its actual magnitude, but from the difference between the temperature of the body and that of the surrounding medium or, otherwise stated, the temperature of the surrounding medium which is chosen is that at the beginning of the temperature reading. The application to a sphere of the theory of cooling or heating of bodies leads to the following important conclusion. The temperature

TABLE I
CHANGES OF TEMPERATURE IN THE CENTER OF A SPHERE

$\frac{at}{R^2}$	$\theta'm$ (%)	$\frac{at}{R^2}$	$\theta'm$ (%)
0.000	100	0.160	41
0.004	100	0.196	29
0.016	100	0.240	19
0.032	100	0.256	16
0.036	99	0.320	9
0.064	91	0.400	4
0.080	83	0.800	0
0.100	71	0.000	0

of the center of the sphere changes in such a manner that, at any given instant of the process, the value: $\frac{at}{R^2}$ (where a is the heat conductivity and t is the time elapsed from the beginning of the process) is equal for all spheres, independent of their sizes and materials. By like or homochronic instants are meant those moments at the beginning of which the difference in temperatures of the center and the surrounding medium reaches the same proportion of the original temperature. The proportion of original temperature, expressed in percentage, is designated by θ_m . The constancy of the value: $\frac{at}{R^2}$, shows that the durations of cooling or heating of two spheres of equal size and unlike materials are inversely proportional to the coefficient of thermal conductivity of these materials; in other words, "the temporary magnitudes of the processes are inversely proportional to the coefficients of thermal conductivity"⁸. It follows from the foregoing discussion that the value of $\frac{at}{R^2}$ can be once and for all calculated for definite moments of the process, i. e., for the designated values of θ_m , which prove to be justifiable for any spheres. These calculations were made by Williamson and Adams¹⁰ and their data were taken from the work of Gröber^{8, 9}. In recalculating our measurements, use was made of tables and curves for temperature changes in the center of a sphere, which were computed by the above named investigators for a case most closely corresponding to that of rubber, where the ratio of the coefficient

of heat transfer to the thermal conductivity is very great. This table and the curve derived from it are shown here because of their great practical significance. The table, constructed in connection with the determination of homochronicity, does not show the actual values of the difference of temperatures but expresses these values in percentage of the original magnitude of this difference. The curve

(Figure 1) makes it possible to determine the value of $\frac{at}{R^2}$ from the known θ'_m .

Thus, if the radius of sphere R and the time t required for cooling or heating of the center of a sphere of a given material to θ'_m are known, it is possible to calculate the heat conductivity a of this material.

EXPERIMENTAL PART

Method of Measurement.—The determinations of the thermal conductivity of rubber were made by observing the course of cooling of rubber spheres 60 ± 0.2 mm. in diam., which had been previously heated to 135°C in a specially constructed heater. The heater comprised a brass cylinder 150 mm. high and 290 mm. in diam., provided on the outside surface with a wire winding connected with the municipal electric power plant. The bottom and the side surfaces of the heater were covered with a layer of asbestos 75 mm. thick. The heater with its thermal insulation was placed in a large iron cylinder (350 mm. in height and 300 mm. in diam.); the axis of a propeller-shaped stirrer passed through the bottom of the heater and the cylinder and was revolved by an outside electric motor. Inside the heater was a special support, on which rested three spheres one above the other, each sphere touching the metal at only three points. Figure 2 shows the support with two spheres. After the support with the spheres was installed in the heater, the latter was closed with an asbestos lid and an electric current was passed through the heating coil. Rechecking of the distribution of temperatures along the axis of the heater showed a drop of temperature along the axis of the upper part of the heater. Therefore the experiments were carried out with only two spheres in the heater, placed on the lower and the center shelves of the support. The spheres were formed by cementing two hemispheres with rubber cement and vulcanizing in a special mold. Before joining the two hemispheres, a copper-constantan thermocouple was fitted into one of the hemispheres. To reduce the error connected with transfer of heat through the wires from the center of the sphere, the leads of the thermocouple (0.2 mm. in diam.) were arranged in such a way that a certain section of them rested along the equitemperature surface (Figure 3). After cementing was completed, the spheres were wound with a cord by means of which they could be suspended during the subsequent process of cooling. After 24 hours the spheres were placed in the heater and the thermocouple leads were connected with the galvanometer through a commutator with gliding contacts, whereby the cold soldered joints were placed in a thermostat. The spheres were removed after 30 minutes when the temperature in the center ceased to change. On removing from the heater, the spheres were suspended by the cords in an air chamber at room temperature.

The purpose of the uncovered chamber was merely to protect the spheres from cooling by air currents. The spheres were arranged in the chamber at the same elevation at a considerable distance (not less than 15 cm.) from each other to avoid any heat exchange.

The constant temperature in the chamber was checked by suspending a thermometer between the spheres. The temperature in the center of the cooling sphere was determined at intervals of 5 minutes for the first 20 minutes and at intervals of 10 minutes thereafter.

In plotting of the cooling curves, the time was calculated from the moment of removal of the spheres from the heater. The general view of the installation is shown in Figure 4.

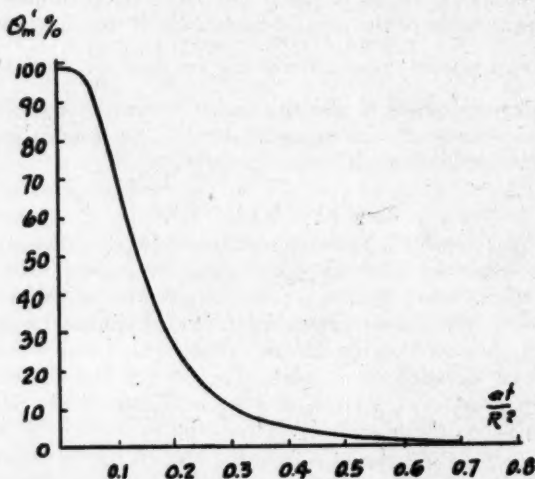


FIG. 1.

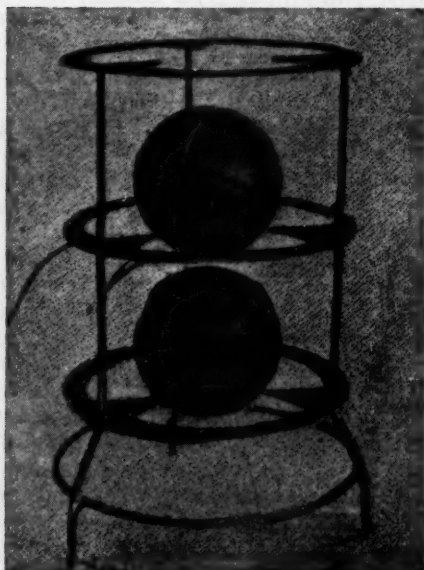


FIG. 2.

The chamber for cooling of the spheres is shown in the right side of the picture. The front wall of the chamber is removed to show the internal arrangement. *Recalculation of the Results of Measurements.* The magnitude determined directly in the experiments is the temperature θ_m of the center of the sphere during

the various moments of its cooling. As an example, the curves of the dependence of θ_m on time for two different mixtures are shown in Figure 5. It was shown in the introduction that the magnitudes $\frac{at}{R^2}$ are equal for different spheres only during the homochronic moments. From the theory of homochronicity it fol-

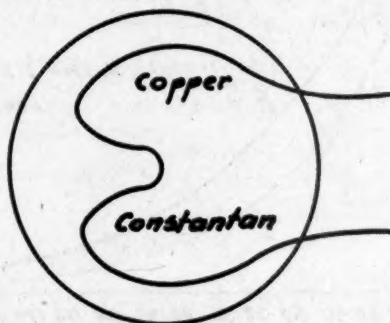


FIG. 3.

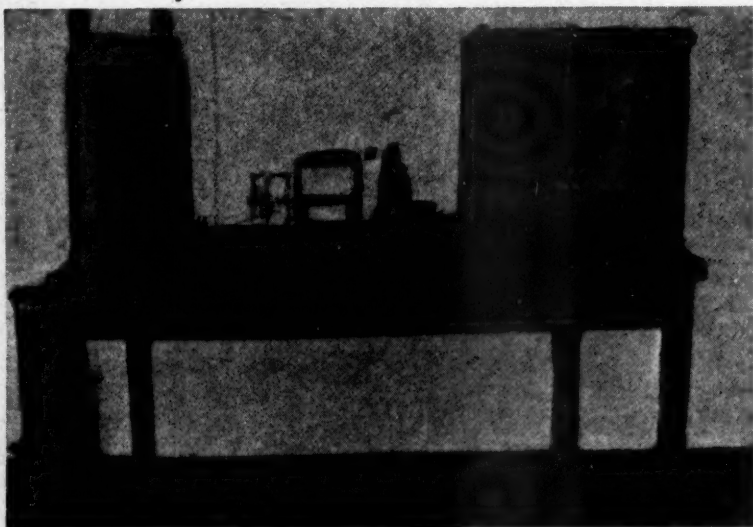


FIG. 4.

lows that the heat of conductivity can be determined by expressing the difference between the temperatures of the center of the sphere and the surrounding medium in percentage of its initial magnitude and by determining the magnitude $\frac{at}{R^2}$ corresponding to this difference from the graph of Figure 1. If the time t which has elapsed from the beginning of cooling of the sphere and the radius of the sphere are known, then it is not difficult to calculate the heat conductivity a .

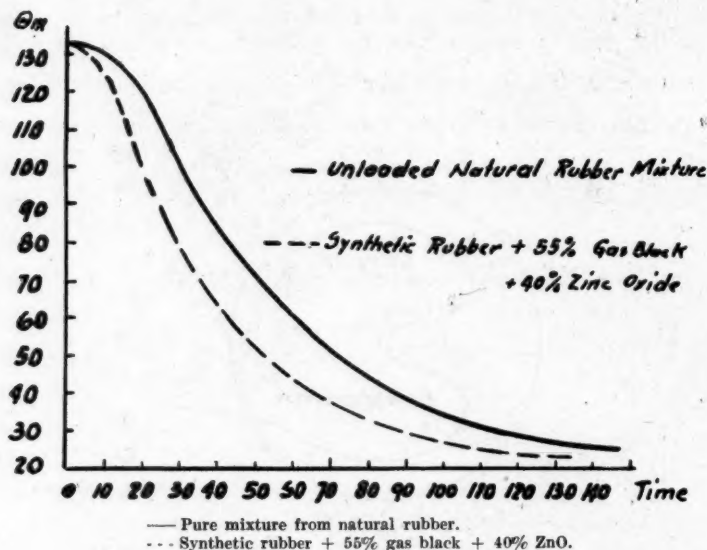


FIG. 5.

The course of temperature decline is shown in Table II and Figure 5.

TABLE II

Time from the beginning of cooling (min.)	Temperature of the center (°C)	Time from the beginning of cooling (min.)	Temperature of the center (°C)
0	133	80	34
5	131	90	30
10	123	100	28
15	113	110	27
20	101	120	24
30	79	130	—
40	64	140	23
50	53	150	—
60	45	160	20
70	39	—	—

Note.—The air temperature θ_z was 18° C. The initial difference of the temperatures was equal to $\theta_m - \theta_{z \text{ initial}} = 115^\circ$ C. To avoid errors, connected with the determination of the magnitude $\frac{at}{R^2}$ from the graph of Figure 1, we used only those values in the Table I and calculated a for those moments of cooling which correspond to values of θ'_m from 9 to 91 per cent. The true temperature of the center of the spheres at those homochronic moments for which a is determined are calculated by the following formula:

$$\theta_m = \frac{(\theta_m - \theta_z)_{\text{initial}} \theta'_m}{100} + \theta_z \quad (2)$$

The magnitudes θ_m , calculated by this formula, are given in Table III.

TABLE III

91	123	29	51.5
83	113.5	19	41
71	99.5	16	36.5
41	65	9	28

The magnitudes θ_m , given in Table III, represent the temperatures of the center of the sphere at the homochronic moments of its cooling, for which the magnitudes $\frac{at}{R^2}$ are known; if the intervals of time t which elapse before the beginning of these homochronic moments (Table IV) are determined from the graph in Figure 5, then we obtain all the required data for calculating the heat conductivity

a. If the value $\frac{at}{R^2}$ is designated by L , then we obtain

$$a = \frac{LR^2}{t} \quad (3)$$

The magnitude a can be easily calculated if in Equation (3) the values for L from Table I and their corresponding values for t from Table III are substituted and radius R is known (for the sphere of the prepared mixture $R=3$ cm.). Here and in the following lines, a is expressed in absolute units.

Objects of the Measurements.—The basic problem involved in the investigation was the determination of the effect of additions of carbon black and zinc oxide and their combinations on the heat conductivity of rubber mixtures of the tire carcass and tread types. Likewise the effects of various kinds of carbon black on the heat conductivity of similar rubber mixtures were investigated. To compare the effect of zinc oxide and carbon black in mixtures prepared from natural and synthetic rubbers, special measurements were made of the heat conductivity of mixtures from natural rubber.

The carcass-type compositions (1 to 6) were prepared from mixtures of natural and synthetic rubbers and differed only in their zinc oxide contents, which were 1.5, 3, 5, 7.5, 20 and 60 per cent by volume. The last two percentages were included for data on the relation between heat conductivity and zinc oxide content. These mixtures are shown in Figure 6.

The tire tread type mixtures (7 to 10), prepared from synthetic rubber, contained the same proportion of gas black (55 per cent by weight), but different proportions of zinc oxide (1, 3, 5 and 7.5 per cent by volume).

The tire tread mixtures (11 to 15) contained zinc oxide only in the proportions commonly used for the activation of accelerators. They differed in their Maikop carbon black contents, which were 5, 9, 15, 24, 32 and 60 per cent by volume. These are shown in Figure 7.

In addition to these mixtures from synthetic rubber, seven mixtures from natural rubber were prepared: I was a pure mixture, II, III and IV were mixtures containing gas black (5, 20 and 60 per cent by volume) and mixtures V, VI and VII contained 5, 20 and 60 per cent of zinc oxide by volume. These are shown in Figure 9.

The thermal conductivities of rubber mixtures with different kinds of carbon black were studied with the mixtures prepared by the compounding formula 7, in which, instead of the Maikop carbon black, the following blacks were used: Yaroslav, Kudinov, Thermax, Gastex and P-33 (See Figure 14).

All the mixtures were vulcanized in a press at 142° C for 50 minutes with a gradual rise of temperature for 40 minutes. It was previously established that the coefficient of thermal conductivity of rubber is independent of the degree of vulcanization⁵, therefore no other methods of curing were employed. In addition to these mixtures, the heat conductivity was determined for the tire tread mixtures made with synthetic rubber and containing various kinds and proportions of carbon black.

Were the heat conductivity k and heat capacity c of rubber independent of the temperature, then its thermal conductivity a would vary but slightly with changes in temperature in connection with changes in the density γ . As far as we know, no information on the dependence of heat conductivity of rubber on temperature is available in the literature. However, published data show that the heat conductivity of poor heat conductors increases with increase in temperature⁶. With respect to the dependence of specific heat capacity on temperature,

TABLE IV

Exp. No.	L	θ_m (°C)	t (sec.)	Thermal conductivity according to Equation (8)
1	0.064	123	630	$a_1 = \frac{0.064 \times 9.45}{630} = 0.000960$
2	0.080	113.5	882	$a_2 = \frac{0.080 \times 9.45}{882} = 0.000868$
3	0.100	98.5	1260	$a_3 = \frac{0.100 \times 9.45}{1260} = 0.000734$
4	0.160	65	2340	$a_4 = \frac{0.160 \times 9.45}{2340} = 0.000646$
5	0.196	51.5	3090	$a_5 = \frac{0.196 \times 9.45}{3090} = 0.000599$
6	0.240	41	3930	$a_6 = \frac{0.240 \times 9.45}{3930} = 0.000577$
7	0.256	36.5	4440	$a_7 = \frac{0.256 \times 9.45}{4440} = 0.000545$
8	0.320	28	6060	$a_8 = \frac{0.320 \times 9.45}{6060} = 0.000499$

the literature contains experimental data¹¹, related only to pure rubber hydrocarbon, which shows that c increases with temperature. In the work described here, c was determined at temperatures not exceeding 47° C. In a series of other published investigations heat capacities were determined at considerably lower temperatures or the data relate only to its mean values within a certain temperature interval, all of which are of no use in this investigation.

Therefore it could be expected that in the expression: $a = \frac{k}{c\gamma}$, there would be a certain increment of k and c with increase of temperature, whereby an increase of c would have to be partially compensated by a decrease in γ because of thermal expansion.

The relation between the thermal conductivity a and temperature in the center of the sphere was studied from 30 to 120° C by the method described above.

It was difficult to carry out measurements at higher temperatures, because the spheres had to be previously heated for certain periods of time about 15-20° C above the require maximum temperature of the thermal interval studied, and

such high temperatures cause rapid changes in the properties of rubber. The graphs show the relation between thermal conductivity a and temperature θ_m at the center of the sphere. It would be more rational to compare the mean heat conductivity with the mean temperature of the sphere. Since the rate of decrease of temperature of the center of the sphere depends on the heat conductivity of all the layers composing in the sphere, it is obvious that in the method described the mean values of heat conductivity are determined. The difficulties in determining the mean temperature of a sphere necessitate a comparison of the magnitude a with the temperature of the center of the sphere, which appears to be rather conditional. Therefore the curves of the relation between a and θ_m makes it possible to estimate for a definite mixture only the rapidity with which a changes with temperature, and to compare the heat conductivities of different mixtures at equal temperatures at the centers of the spheres, i. e., at close mean temperatures. These mean temperatures differ but little at equal temperatures of the centers of the spheres, because the temperatures of the surrounding medium are nearly equal in all cases.

The effect of zinc oxide and gas black in various proportions in synthetic rubber mixtures on the relation between a and θ_m is shown in Figures 6 and 7. The curves show that the heat conductivities of all mixtures (1-6 and 11-15) increase with temperature. With synthetic rubber-gas black mixtures, this relation is more sharply defined than for the zinc oxide-carcass mixtures. Figure 8 shows the analogous curves for mixtures 7 to 10, containing 55 per cent of gas black and different proportions of zinc oxide. Here the temperature relation of a and θ_m is of the same character. In Figure 9 the curves for natural rubber mixtures show that the increments of a with increase in θ_m for mixtures V to VII containing gas black and for the pure mixture I are less than for the mixtures II to IV containing zinc oxide. Because the heat conductivity of rubber depends on the temperature, the heat conductivity of different mixtures can be more conveniently compared from curves showing the effect of various fillers on the heat conductivity of mixtures at the same temperature. Such curves can be constructed from data on the relation between a and θ_m in the graphs in Figures 6, 7, 8 and 9.

The curves in Figure 10 show the effect of fillers on a in mixtures 1 to 6 and 11 to 15. These graphs refer to temperatures of 50, 75 and 100° C at the centers of the spheres. The abscissa represents the proportions of filler (per cent by volume). The curves show that by addition of zinc oxide up to 3 per cent by volume (16 per cent by weight) to synthetic rubber and natural rubber carcass mixtures the heat conductivity decreases sharply; greater additions of zinc oxide up to 7.5 per cent by volume (40 per cent by weight) result in a comparatively slow rise of a . Increasing additions of gas black up to 15 per cent by volume (25 per cent by weight) produce a substantial rise of a ; further additions of carbon black up to 30 per cent by volume result in a drop of a ; with still greater additions of carbon black (up to 60 per cent by volume) the thermal conductivity remains practically unchanged.

Figure 11 shows that the introduction of zinc oxide into a synthetic rubber mixture containing 32 per cent by volume of gas black (55 per cent by weight) has a different effect from that of zinc oxide in a rubber mixture containing no gas black. Here a small addition of zinc oxide increases a ; greater additions first decrease a and then increase it.

The effects of various proportions of zinc oxide and carbon black to natural rubber mixtures are shown in Figure 12. The graphs show that here too zinc

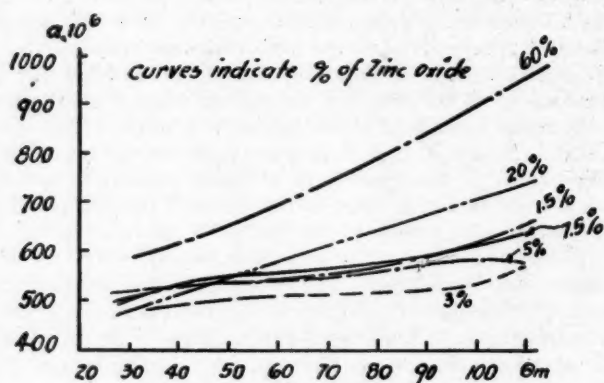


FIG. 6.—Synthetic rubber.

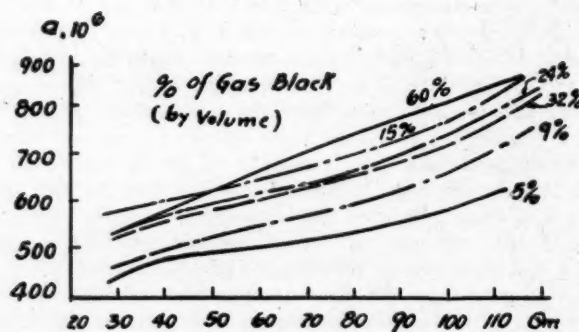


FIG. 7.—Synthetic rubber.

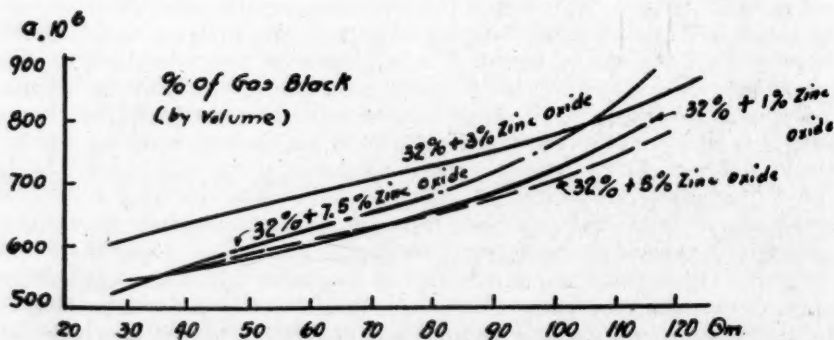


FIG. 8.—Synthetic rubber.

oxide first increases and then decreases the thermal conductivity in contrast to the effect of gas black. The fact that small amounts of zinc oxide decrease the heat conductivity and large amounts increase it whereas gas black has the reverse effect can be explained in the following way for natural rubber mixtures.

It was shown in an earlier paper⁵ that by addition of zinc oxide to natural rubber mixtures the heat conductivity k increases at first slowly and then more rapidly; by addition of gas black the rate of increase of k changes in the opposite

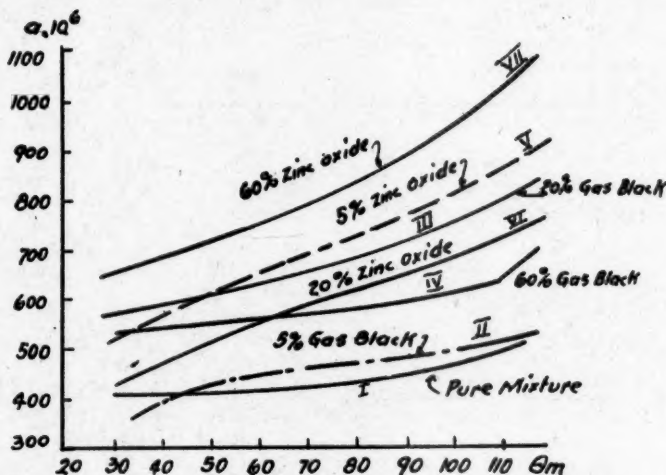


FIG. 9.—Natural rubber.

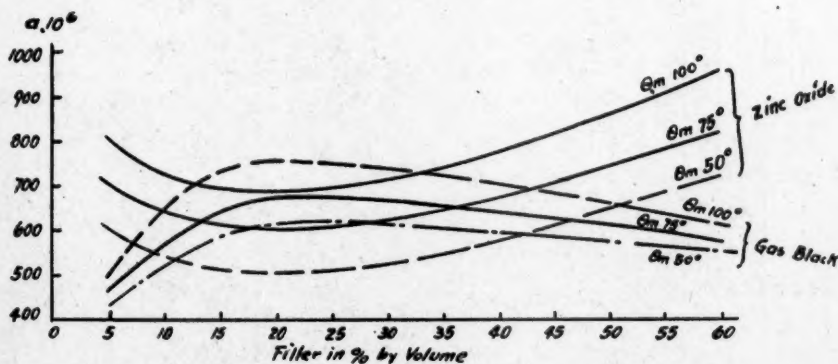


FIG. 10.

way. The density γ increases almost as a straight line function of the volume of filler; zinc oxide has a greater effect than that of carbon blacks. It follows that the addition of zinc oxide to a rubber mixture produces at first a relatively small increment of the numerator and a greater increment in the denominator in the expression: $a = \frac{k}{c\gamma}$, i. e., the heat conductivity decreases. The addition of carbon black to rubber mixtures results in different changes in the factors in the equation above; the reason is chiefly that carbon black and rubber are more

closely related to one another in specific gravity than to zinc oxide. With small additions of carbon blacks, k increases rapidly and γ comparatively slowly; the result is an increase in a . With large additions of carbon blacks, the increase

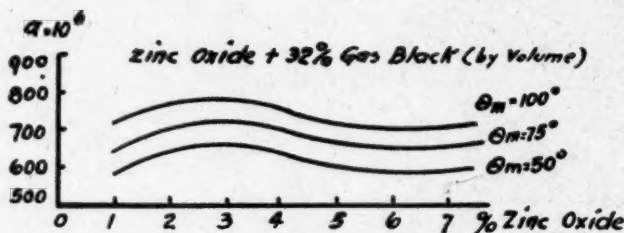


FIG. 11.

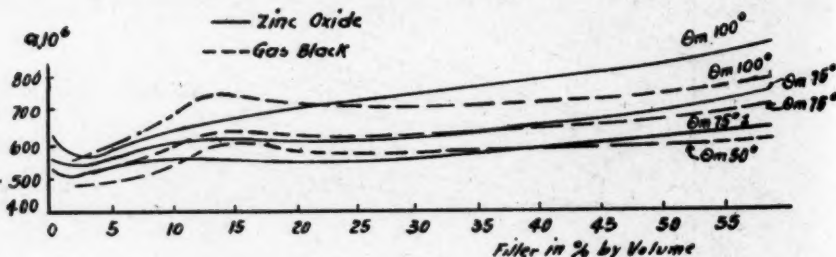


FIG. 12.

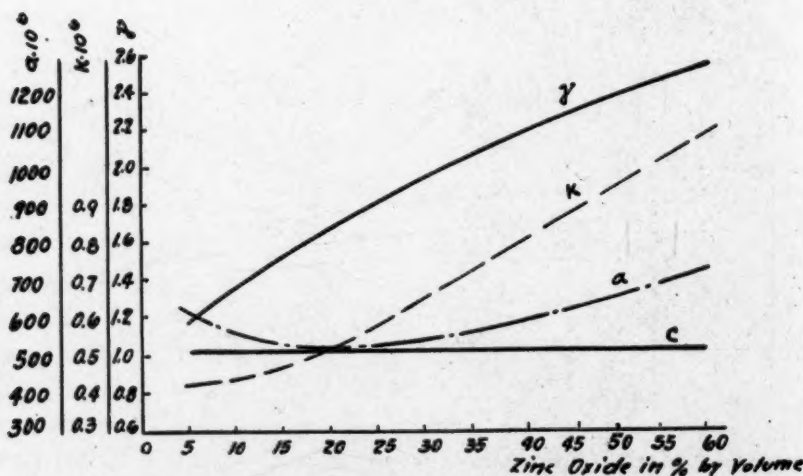


FIG. 13.

in k is retarded and accordingly a begins to decrease. The changes in a , k , γ and c with increases in zinc oxide to natural rubber mixtures are shown in Figure 13. The values for k are taken from data in earlier paper⁵; γ and a were determined in the present work for the same mixtures; the c values were calculated from the corresponding values of a , k and γ .

From a practical point of view, carbon black is the basic filler on which the heat conductivity of tire treads depends. Therefore a comparative study was

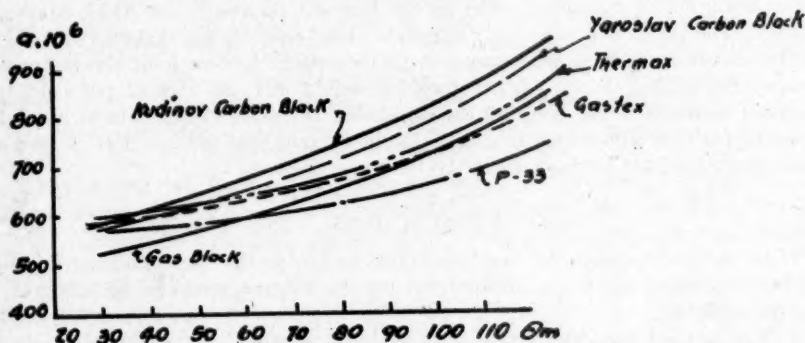


FIG. 14.

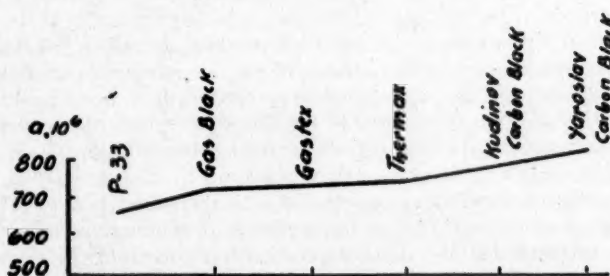


FIG. 15.

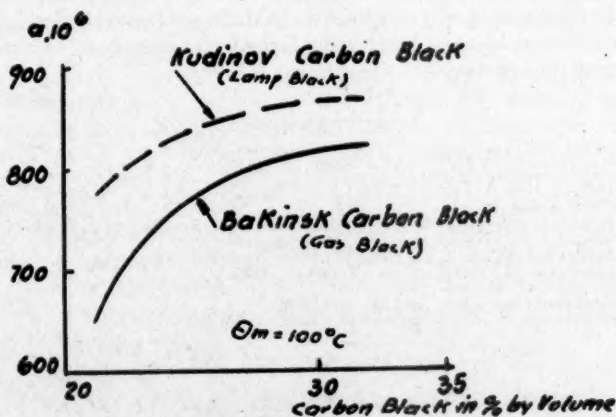


FIG. 16.

made of the a values for synthetic rubber mixtures, which differ only in the kind of carbon black added. The curves in Figure 14, which show the relation between a and θ_m of tire tread mixtures containing different kinds of carbon black indicate that this dependence is less well defined with Thermax, Gastex and P-33 than

with Yaroslav, Kudinov and Maikop carbon blacks. The curves in Figure 15 show the effect of different kinds of carbon black in the increasing order of their effects on the heat conductivities of rubber mixtures for $\theta_m = 100^\circ \text{C}$. In this series the order of increasing effect on the heat conductivity was: P-33, Maikop, Gastex, Thermax, Kudinov and Yaroslav. For different θ_m values, the order of the carbon blacks did not change. A further study was made of the comparative effects of 36, 45 and 54 per cent by weight (21, 26 and 32 per cent by volume) of Bakinsk and Kudinsk carbon blacks in tire tread mixtures of a different composition. The curves in Figure 16 show again that for $\theta_m = 100^\circ \text{C}$, lamp-black gave a higher heat conductivity than gas black.

CONCLUSIONS

1. In rubber technology, the important factor is the heat conductivity of rubber mixtures, which is characterized by the rate of temperature change of the inner layers.

2. The method proposed makes it possible to compare the heat conductivities of rubber mixtures.

3. The heat conductivities of all types of rubber mixtures increase with increase in temperature.

4. Addition of zinc oxide in the usual proportions decreases the heat conductivity of mixtures containing no carbon black; in mixtures containing carbon blacks the addition of zinc oxide increases slightly their heat conductivity. It follows that the addition of zinc oxide for the acceleration of the vulcanization process has an insignificant influence on thermal conductivity.

5. With increasing additions of carbon black up to 25 per cent by weight of the rubber mixtures result the heat conductivity increases; but with further increases in the percentage of carbon blacks the heat conductivity decreases.

6. Rubber mixtures of the same composition but containing different kinds of carbon black show different heat conductivities. The lowest heat conductivity was found in rubber mixtures containing P-33 carbon black, followed in increasing order of heat conductivity by mixtures with Maikop, Gastex, Thermax, Kudinov and Yaroslav carbon blacks. Thus lampblacks have a greater effect on the heat conductivity of rubber mixtures than do gas blacks.

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OXIDATION OF VULCANIZED RUBBER

EFFECT OF TEMPERATURE, STATE OF CURE, AND THICKNESS *

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Accelerated aging tests based either on exposure of rubber to heated air or oxygen under variant pressures are now used in every rubber laboratory in the world. These tests have been an important factor in bringing increased serviceability of rubber goods in recent years.

Within the last few years a number of papers have been published dealing with the mechanism of oxidation of vulcanized rubber^{5, 6, 8, 13, 14}. In several of them the quantity of oxygen absorbed is correlated with the degree of physical deterioration. These studies are particularly timely because of the need in the rubber manufacturing and consuming industries for more rapid accelerated-aging tests than those which have been considered standard since Geer⁷ suggested the air oven test and Bierer and Davis⁴ the oxygen pressure test. However, since so many sets of conditions are now being considered for use in aging tests, it is important that careful studies be made of the effect of the many variables on the aging mechanism.

The present authors⁸ previously reported an investigation of the rate of oxidation of soft vulcanized rubber at 60°, 70° and 80° C. Over this temperature range there appeared to be no change in the mechanism of oxidation. A temperature coefficient of deterioration of 2.38 per 10° C. change in temperature was found. It was also found that, following a short induction period of oxidation during which the tensile strength of the rubber may actually increase, the tensile strength decreases as a linear function of the quantity of oxygen absorbed.

This investigation is a continuation of the work previously reported. The rate of oxidation was studied at 90°, 100° and 110° C. In addition, the effect of state of cure and thickness on the rate of oxidation at 80° C. was investigated.

The same apparatus and technique were employed in most of this work as in the previous study. Standard tensile-specimens of vulcanized rubber, after drying and weighing, were suspended in a small pressure vessel under an original oxygen pressure of 60.9 ± 0.4 inches (154.7 ± 1.0 cm.) of mercury absolute for varying periods of time at 90°, 100°, and 110° C. The progress of oxidation was followed by means of a recording pressure gage. When oxidation had progressed to the desired extent, the specimens were removed from the vessel, weighed, and tested for tensile strength and elongation at break. The values obtained were compared with those obtained on unoxidized, dry specimens which were tested at the same time.

PREPARATION OF COMPOUNDS AND PROCEDURE

Three rubber compounds were used (Table I). Compounds 1 and 2 were employed in the previous investigation. Compound 2 differs from compound 1 in that it contains 1 part of a commercial antioxidant, phenyl- α -naphthylamine.

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In compound 3 the antioxidant is eliminated and 3 parts of tetramethylthiuram disulfide are substituted for the sulfur and di-*o*-tolylguanidine.

In the preparation of the compounds and molded sheets the procedure recommended by the Physical Testing Committee of the American Chemical Society¹ was followed.

For the studies involving effect of temperature, sheets of compound 1 were molded about 15.2 cm. square and 0.19 cm. thick and vulcanized for exactly 40 minutes at 142° C. Sheets of compound 3 of the same dimensions were cured for 60 minutes at 142° C. Sheets of compound 1 of the same dimensions were vulcanized for 25, 40, 80 and 150 minutes at 142° C. for the studies involving state of cure. For the investigation of the effect of thickness on oxidation rate, sheets of compound 2 about 15.2 cm. square and 0.043 cm., 0.084 cm., 0.140 cm. and 0.190 cm. thick were vulcanized for 40 minutes at 142° C.

TABLE I
COMPOSITION OF COMPOUNDS

Materials	Compounds		
	1	2	3
Smoked sheet	100.00	100.00	100.00
Zinc oxide	20.00	20.00	20.00
Sulfur	3.00	3.00	—
Di- <i>o</i> -tolylguanidine	0.75	0.75	—
Phenyl- α -naphthylamine	—	1.00	—
Tetramethylthiuram disulfide	—	—	3.00
	123.75	124.75	123.00

The time of cure for compounds 1 and 2 (40 minutes at 142° C.) was selected to give slightly less than maximum tensile strength. The 25-minute cure is an undercure, and the 80- and 150-minute cures are overcures. The A. S. T. M. type C die² was used for cutting test-specimens. The same stainless-steel pressure vessel previously used was employed in these studies. Average tensile strength and elongation were calculated in accordance with the A. S. T. M. procedure for evaluating aging effects³.

For the oxidation studies carried out at 80° C., the pressure vessel was immersed in a water bath. For the work carried out at 90°, 100° and 110° C., a glycerol bath was substituted for the water bath. The bath was equipped with controls to maintain a variation not in excess of $\pm 1^\circ$ C. Details of the procedure followed in these studies were described previously.⁸

EFFECT OF TEMPERATURE ON RATE OF OXIDATION

Test-specimens of compound cured for 40 minutes were aged for periods of 6 to 24 hours at 90° C., 2 to 18 hours at 100°, and 2 to 7 hours at 110°. The values obtained for oxygen absorption, determined by weight gain and by pressure loss in the apparatus, are given in Table II, and also tensile strength and elongation values determined on the aged specimens and unaged controls. The course of oxidation at the three temperatures, determined by weight gain, is plotted in Figure 1. The values previously obtained at 60°, 70° and 80° C. are also plotted for comparison. The values for weight gain are used for purposes of discussion; they are considered more reliable because volatile oxidation products are believed to affect pressure readings to some extent.

It was found previously⁸ that the course of oxidation at 60°, 70° and 80° C. varied essentially as straight-line functions with time of aging over the oxidation range investigated. The data obtained for oxidation at 90° C. also appear to fall along a straight line. However, the data obtained for oxidation at 100° C. and 110° C. appear to fall along curves which incline toward the abscissa as oxidation progresses. These results may indicate that under the conditions of these tests

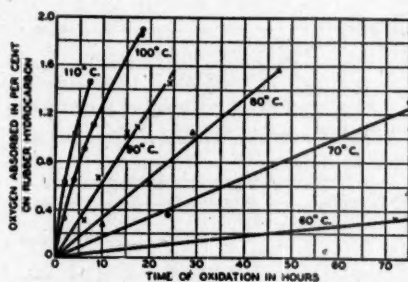


FIG. 1.—Rate of oxidation of compound 1 at 60° to 110° C. as determined by weight gain.

TABLE II

EFFECT OF TEMPERATURE ON OXYGEN ABSORPTION AND PHYSICAL DETERIORATION

Temp. of oxidation (° C.)	Time of oxidation (Hrs.)	Oxygen absorption on rubber hydrocarbon		Tensile strength (Kg. per sq. cm.)	Elonga- tion (%)
		By weight gain (%)	By pressure loss (%)		
90	6	0.32	0.27	227.1	720
90	9	0.67	0.63	186.6	705
90	15	1.03	1.03	117.4	660
90	17	1.09	0.96	101.9	690
90	24	1.45	1.21	63.6	640
			Control av.	266.4	700
100	2	0.33	0.31	199.7	715
100	4	0.65	0.60	147.6	710
100	6	0.91	0.77	112.8	680
100	8	1.09	0.98	70.7	670
100	17.75	1.86	1.78	5.1	410
100	18	1.90	1.70	6.3	395
			Control av.	267.8	700
110	2	0.63	0.49	153.3	680
110	4	1.03	0.85	46.4	565
110	7	1.46	1.25	10.5	370
			Control av.	266.0	685

there was a critical temperature between 90° and 100° C. beyond which sufficient oxygen was not available for oxidation to take place uniformly at the expected rate. It is believed that the rate of diffusion of oxygen into the rubber was too low at 100° and 110° C. for oxidation to take place at its normal rate. However, there is also the possibility of a change in oxidation mechanism—for example, the decomposition of peroxides before they become effective in activating additional molecules of rubber for oxidation.

The former suggestion receives some support from the fact that on repeating the oxidation experiments at 100° and 110° C. with thinner specimens 0.084 cm.

thick), the rate of oxidation increased, but as oxygen absorption increased beyond 0.60 per cent the change in oxidation rate followed that of the thicker specimens.

In our previous investigation of oxidation at 60°, 70° and 80° C. it was found that the autocatalytic nature of the oxidation process was almost negligible over the oxidation range investigated. In the investigation here reported it was found that the autocatalytic effect was also of little consequence over the oxidation range investigated. This is in agreement with results by Morgan and Naunton¹⁴.

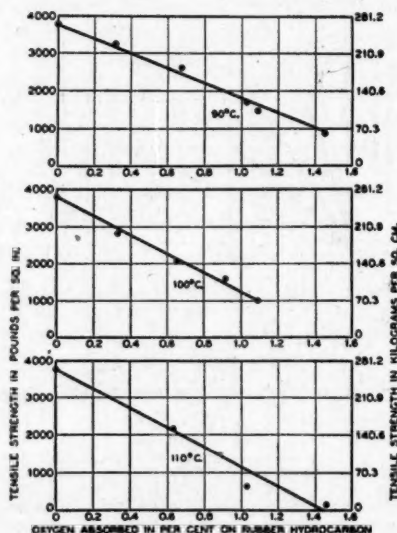


FIG. 2.—Effect of oxygen absorbed at three temperatures on tensile strength of compound 1.

TABLE III

OXYGEN ABSORPTION AND TIME OF OXIDATION EQUIVALENT TO A DECREASE IN TENSILE STRENGTH TO 140.6 KG. PER SQ. CM. AT VARIOUS TEMPERATURES

Temp. of oxidation (° C.)	Time of oxidation (Hrs.)	Oxygen absorption, weight gain on hydrocarbon (%)
60	203.00	1.30
70	80.00	1.17
80	32.50	1.08
90	12.5	0.83
100	4.50	0.71
110	2.10	0.65

Figure 2 shows the variation in tensile strength of the rubber with progressive increase in oxygen content, determined by weight gain. The decrease in tensile strength for the addition of a given amount of oxygen increases as the temperature of oxidation increases. This was also found to be true in the previous investigation of oxidation over the range of 60° to 80° C. In each case the loss in tensile strength appears to be a straight-line decrease with increase in weight or absorption of oxygen.

The quantity of oxygen found by weight gain to be equivalent to a decrease in tensile strength to 140.6 kg. per sq. cm. (2000 pounds per square inch) over the entire temperature range thus far investigated is shown in Table III and

plotted in Figure 3. This decrease in tensile strength is taken as approximately a 50 per cent deterioration in physical properties. The plotted data indicate that the quantity of oxygen equivalent to a tensile strength deterioration of about 50 per cent varies as a straight-line function of the temperature at which oxidation take place.

It appears that the variation in the measured oxygen absorption for a given deterioration at different temperatures of aging is the result of an increase in a secondary reaction. The total over-all weight variation involved for a 50 per cent deterioration between 60° and 110° C. aging in our tests was only about 0.12 gram. As a result of his investigations of the oxidation of vulcanized rubber at 80° C., Kohman¹¹ suggested that in the mechanism of oxygen absorption two separate reactions are involved; one consists of oxygen adding to the double bonds of the rubber molecule and another a breaking down of the oxidized molecule. The rate of the decomposition reaction would be expected to increase as the

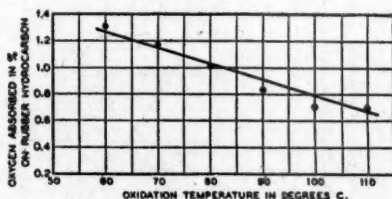


FIG. 3.—Oxygen required to cause deterioration to 140.6 kg. per sq. cm. (compound 1).

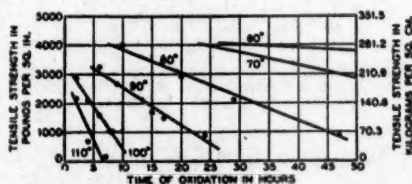


FIG. 4.—Variation in tensile strength of compound 1 with time of oxidation at 60° to 110° C.

temperature increased. It is believed that the oxidation products evolved are probably water for the most part, along with small amounts of carbon dioxide, aldehydes and acidic materials. The surface of the P_2O_5 in desiccators over which the aged specimens of rubber were stored turned brown, probably as a result of the absorption of some of the volatile oxidation products other than water. Kohman observed the condensation of drops of water which were strongly acidic in the cool parts of his apparatus during the latter stages of oxidation. Williams and Neal¹⁰ reported the presence of oxidation products at 25° C. which were absorbed by solid sodium hydroxide. Kemp, Bishop and Lasselle⁹ found carbon dioxide, water, formic acid and formaldehyde resulting from the oxidation of raw rubber and gutta-percha hydrocarbon.

Although the oxidation-rate curves of Figure 1 appear to indicate that no change in mechanism of oxidation takes place until a temperature of 90° C. is exceeded, the data plotted in Figure 3 may be taken to indicate that the oxidation mechanism is changing continuously as the temperature is raised. For this

reason caution should be exercised in specifying temperature conditions for accelerated aging tests unless the conditions are chosen on the basis of correlation with conditions of service.

The variation in tensile strength with time of aging at the various temperatures investigated is shown in Figure 4. The periods of time required for a deterioration to 140.6 kg. per sq. cm. tensile strength are recorded in Table III. When these time values are plotted logarithmically as ordinates with the oxidation temperature on a Cartesian scale, a straight-line variation is ob-

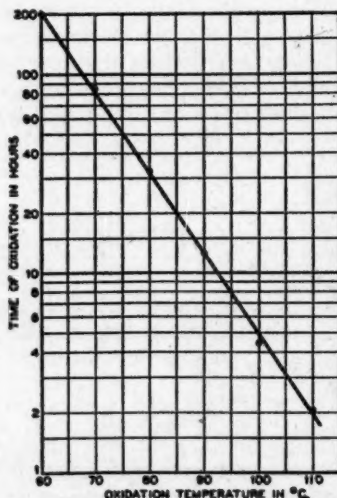


FIG. 5.—Time-temperature oxidation relation for deterioration of tensile strength of compound 1 to 140.6 kg. per sq. cm.

TABLE IV

EFFECT OF HEATING IN CARBON DIOXIDE ON CHANGE IN WEIGHT AND PHYSICAL PROPERTIES

Temp. (° C.)	Time (Hrs.)	Weight loss on rubber hydrocarbon (%)	Tensile strength (Kg. per sq. cm.)	Elonga- tion (%)
80	32.5	0.003	296.7	690
110	2	0.055	307.6	700
			Control 274.5	670

tained. This is shown in Figure 5 where the values obtained in the previous investigation at 60°, 70° and 80° C. are also included. The plotted data show that over the entire temperature range of 60° to 110° C. the rate of deterioration is doubled for each 7.5° C. increase in temperature. This corresponds to a temperature coefficient of deterioration of 2.5 for each 10° C. change in temperature. A coefficient of 2.38 was previously reported for the range 60° to 80° C.

In an effort to determine the effect of temperature alone on the physical characteristics of the rubber, test runs were made with dried tensile-specimens in an atmosphere of carbon dioxide for 32.5 at 80° and for 2 hours at 110° C. These periods correspond to the time required for approximately a 50 per cent tensile

deterioration when aging is carried out in oxygen at 80° and 110° C. Assuming a temperature coefficient of vulcanization of 2.5 for each 10° C. rise in temperature, these heating periods would be equivalent to increasing the time of vulcanization by about 8 minutes. Figure 6 shows that no physical deterioration would be expected from this amount of heating. In these tests oxygen was not entirely eliminated but was reduced to a partial pressure of about 0.2 mm., calculated to test temperature. The method followed was to bring the apparatus up to the desired pressure with carbon dioxide, release and then refill; this process was repeated ten times previous to starting the test.

In both test runs there was a slight loss in weight rather than a gain. In the run at 80° C. the loss was 0.6 mg., and at 110° C., 10 mg. on about 18 grams of rubber hydrocarbon content in each case. In both cases there was an increase in tensile strength and elongation over that of the control specimens. The data concerning these tests are given in Table IV. It may be assumed that the improvement in physical characteristics is due to aftervulcanization. These results

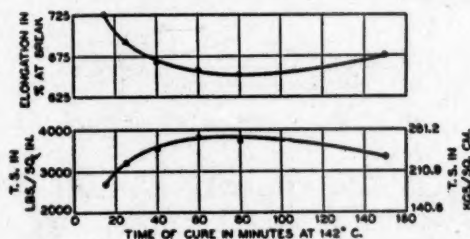


Fig. 6.—Effect of time of cure on tensile strength and elongation of compound 1.

are in agreement with those of Dufraisse and Etienne⁶, who found that specimens stored in a vacuum at 80° C. as controls in their oxidation studies increased in tensile strength.

EFFECT OF STATE OF CURE ON OXIDATION RATE

To determine the effect of time of vulcanization on the rate of oxygen absorption, tensile test specimens cut from sheets which had been cured for 25, 40, 80 and 150 minutes at 142° C. were aged for various periods of time at 80° C. Figure 6 gives the variation in tensile strength and in elongation at break for the compound over a range of cures. Figure 7 shows the variation in free sulfur content with time of vulcanization. The values plotted in these figures are given in Table V.

TABLE V

VARIATION IN PHYSICAL CHARACTERISTICS AND FREE SULFUR CONTENT WITH TIME OF VULCANIZATION

Time of vulcanization at 142° C. (Min.)	Tensile strength (Kg. per sq. cm.)	Elongation (%)	Free sulfur content (%)
15	189.0	724	—
25	224.9	692	1.11
40	248.3	668	0.74
60	268.2	658	—
80	261.8	652	0.14
150	235.4	676	0.024

The course of oxidation for the various cures, determined by weight gain, is shown in Figure 8. The oxygen absorption and accompanying physical test data are given in Table VI. The data show that, for the compound investigated, the rate of oxidation increases rapidly as time of cure is increased. For the undercure (25 minutes at 142° C.) and for the technical cure (40 minutes at 142° C.) the

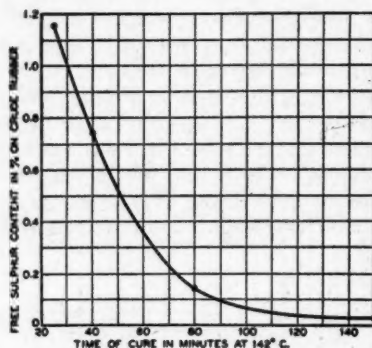


FIG. 7.—Effect of time of vulcanization on free sulfur content of compound 1.

TABLE VI

EFFECT OF TIME OF VULCANIZATION ON RATE OF OXIDATION AND DETERIORATION OF PHYSICAL PROPERTIES

Time of vulcanization at 142° C. (Min.)	Time of oxidation at 80° C. (Hrs.)	Oxygen absorption on rubber hydrocarbon		Tensile strength (Kg. per sq. cm.)	Elongation at break (%)
		By weight gain (%)	By volume loss (%)		
25	17	0.20	0.20	279.4	765
25	24	0.32	0.23	280.5	820
25	31	0.42	0.39	237.6	760
25	Control	—	—	261.5	730
40	7	0.12	0.13	282.6	725
40	17	0.44	0.38	233.7	710
40	30	0.86	1.06	171.5	685
40	Control	—	—	282.6	705
80	7	0.40	0.30	195.8	615
80	17	1.39	1.30	67.8	460
80	23	1.94	1.80	22.8	315
80	Control	—	—	266.1	640
150	4	0.49	0.39	101.6	525
150	7	1.22	1.09	20.4	300
150	11	1.71	1.57	17.6	300
150	Control	—	—	236.6	650

rate of oxygen absorption appears to be a straight-line function of the time of aging. For overcures (80 minutes and 150 minutes at 142° C.) the rate appears to be accelerated as aging progresses. On the basis of the points shown in Figure 8, it might be assumed that the oxidation rate curves intercept the time axis other than at the origin. The recording pressure charts, however, show that the pressure decreased uniformly from the start.

The accelerated or autocatalytic oxidation effect is indicated more definitely in Figure 9, where the data for quantity of oxygen taken up in 5, 10, 15, and 20 hours of aging at 80° C., determined by weight gain, are plotted with time of vulcanization as the other variable. These curves show a rapid increase in the rate of oxidation, even in a 5-hour oxidation period for cures of more than 40 minutes at 142° C. These results do not support the suggestion of Morgan and Naunton¹⁴ that the autocatalytic effect begins to be apparent only after all of

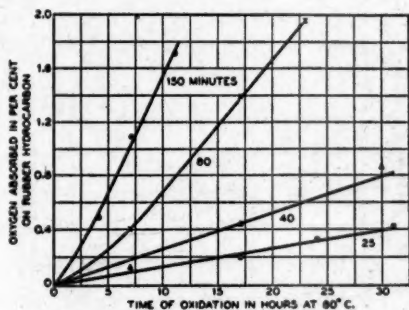


Fig. 8.—Effect of time of vulcanization on rate of oxygen absorption of compound 1.

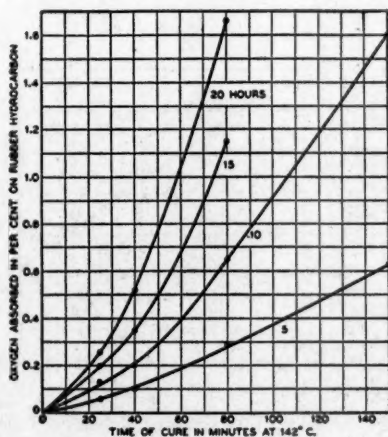


Fig. 9.—Effect of time of cure on quantity of oxygen absorbed in definite aging periods at 80° C.

the antioxidant is consumed. It is not likely that all of the antioxidant would be consumed in the short oxidation period required to show this autocatalysis.

The effect of time of vulcanization on deterioration in tensile strength for given quantities of oxygen absorbed is shown in Figure 10. It is apparent that tensile strength decreases as a straight-line function of time of cure with the absorption of a given quantity of oxygen. The upper curve in Figure 10 represents the tensile strength of the compound after it was dried but unaged, and may be taken as the control. This curve shows that tensile strength increases to a maximum at about 40-minute vulcanization. Reference to the other curves in

Figure 10 show that after oxidation, even to 0.3 per cent oxygen content, tensile strength decreases progressively more as the time of vulcanization of the rubber is extended.*

These results are not in agreement with those reported recently by Dufraisse and Etienne⁶, who studied a diphenyl-guanidine-accelerated compound somewhat similar to that used in our studies. Although they agree that it is always advantageous to undercure in the vicinity of the optimum cure rather than to overcure, they state that oxidizability does not increase indefinitely as a function of the time of vulcanization but rather becomes fairly constant or even decreases with cures somewhat beyond optimum. This is not only contrary to

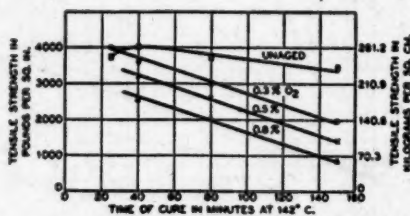


FIG. 10.—Effect of time of vulcanization on deterioration in tensile strength of compound 1 with absorption of definite quantities of oxygen at 80° C.

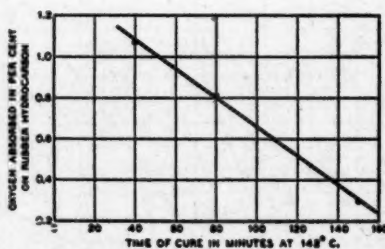


FIG. 11.—Oxygen required to cause deterioration to 140.6 kg. per sq. cm. at 80° C. when time of cure is varied (compound 1).

the results which we have obtained but is also contrary to the general experience of rubber technologists.

The results of our investigation are in accord with those of Marzetti¹², Kirchhoff¹⁰, Stevens¹³ and Kohman¹¹, who showed that the higher the degree of cure, the more rapid is the rate of absorption of oxygen, and with the experience of rubber technologists in industry.

The time of vulcanization also has an important bearing on the quantity of absorbed oxygen, which corresponds to a definite physical deterioration. Figure 11 shows that the quantity of oxygen corresponding to a deterioration in tensile strength to 140.6 pounds per square inch decreases rapidly as time of cure increases. For a good technical cure the quantity required is about 1 per cent; for an extreme overcure (150 minutes) the quantity of oxygen required is only about 0.30 per cent. The point in this plot representing oxygen required in the 40-minute cure was taken from an extended plot of the data given in Table VI.

EFFECT OF THICKNESS ON RATE OF OXIDATION

Williams and Neal¹⁶ reported that oxygen absorption curves obtained at 100° C. with rubber containing no antioxidant failed to show a uniform rate of oxidation, which their studies indicated to be due to a deficiency of oxygen within the rubber. They also showed that such a deficiency occurred in strips of rubber 4 mm. (0.157 inch) square, oxidized at 26° C. In these studies the starting oxygen pressure was atmospheric and decreased as oxidation proceeded.

To determine the effect of thickness on the rate of oxidation at 80° C. and 3.5 kg. per sq. cm. (50 pounds per square inch) oxygen pressure, a study was made with compound 2. This compound, containing 1 per cent of phenyl- α -naphthylamine as antioxidant, was used to avoid too rapid a rate of deterioration. Tensile test specimens cut from molded sheets approximately 0.43, 0.84, 1.40, and 1.90 mm. (0.017 to 0.075 inch) were used. Oxidation was carried out in accordance with

TABLE VII
EFFECT OF THICKNESS ON RATE OF OXIDATION

Time of aging (Hrs.)	Thickness of specimens (Cm.)	Weight gain on rubber hydrocarbon (%)	Tensile strength		Elongation	
			Unaged	Aged	Unaged	Aged
			(Kg. per sq. cm.)		(%)	(%)
48	0.043	0.63	267.8	229.9	680	680
	0.084	0.63	269.2	224.3	680	670
	0.140	0.63	266.1	226.4	680	680
	0.190	0.64	265.8	224.6	685	680
	Average 0.63		267.1	226.3	681	678
96	0.043	1.04	267.8	147.3	680	625
	0.084	1.09	269.2	154.3	680	620
	0.140	1.20	266.1	157.5	680	630
	0.190	1.18	265.8	145.5	685	615
	Average 1.13		267.1	151.1	681	625
144	0.043	1.49	267.8	115.6	680	610
	0.084	1.50	269.2	111.4	680	600
	0.140	1.52	266.1	113.5	680	585
	0.190	1.57	265.8	112.5	685	580
	Average 1.52		267.1	113.3	681	594

the usual accelerated aging procedure⁸, except that a temperature of 80° C. and an oxygen pressure of 3.5 kg. per sq. cm. were employed. The aging periods were 48, 96, and 144 hours. Six tensile specimens of each thickness were aged simultaneously, making a total load of about 50 grams of compound or 36 grams of rubber hydrocarbon. The total oxygen available in the apparatus was about 29 grams.

Oxygen absorption was determined by weight gain alone, pressure being maintained as nearly uniform as is usual in accelerated aging tests due to the large excess present.

The gains in weight and decreases in tensile strength and elongation at break which resulted from aging are given in Table VII. The variation in test results with variation in thickness is very slight and may be considered as negligible. The results indicate that under the conditions of the test there is no variation in rate of oxidation or rate of deterioration in tensile strength with variations in thickness of test specimens from 0.43 to 1.90 mm. With this compound a deterioration of 140.6 kg. per sq. cm. occurs with the addition of 1.3 per cent of

oxygen, which corresponds exactly with the value reported in previous oxidation studies on this compound⁶. This value of 1.3 per cent of oxygen compares with a value of about 1.08 per cent obtained on the compound containing no antioxidant. This difference may be due to oxygen taken up by the antioxidant.

AGING OF RUBBER VULCANIZED WITH TETRAMETHYLTHIURAM DISULFIDE

It is generally known that rubber compounds vulcanized with tetramethylthiuram disulfide alone are very resistant to oxidation. For this reason it appeared desirable to determine if the mechanism of oxidation of such a compound was different from that of a rubber compound vulcanized with sulfur and accelerated.

Tensile specimens of compound 3 were oxidized at 80° C. for periods of 504 and

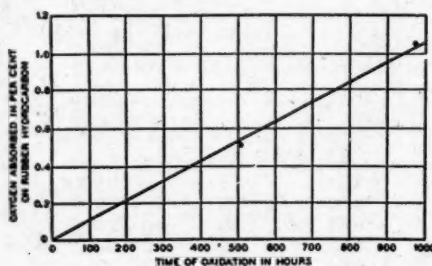


Fig. 12.—Rate of oxidation of compound 3 at 80° C.

TABLE VIII

OXYGEN ABSORPTION AND PHYSICAL DETERIORATION OF COMPOUND 3 AT 80° C.

Time of oxidation (Hrs.)	Oxygen absorption on rubber hydrocarbon		Tensile strength (Kg. per sq. cm.)	Elongation (%)
	By weight gain (%)	By pressure loss (%)		
504	0.51	0.57	144.1	720
978	1.05	1.17	49.9	660
Control	—	—	235.5	670

978 hours. The molded sheets from which the specimens were cut were vulcanized for 60 minutes at 142° C. This represent a 300 per cent overcure since the technical cure is 15 minutes at 142° C. The tensile strength for the 60-minute cure was about the same as for the 15-minute cure. Data showing the rate of oxidation are plotted in Figure 12, and pertinent data are given in Table VIII.

The rate of oxidation of this compound was found to be very low as compared with that of the other compounds investigated. As with the other compounds, the quantity of oxygen absorbed under the conditions of the test varied as a straight-line function of the time of oxidation. The mechanism of oxidation appears to be the same as that of compounds vulcanized with sulfur except that the rate is lower.

The quantity of absorbed oxygen, determined by weight gain to be equivalent to a deterioration in tensile strength to 140.6 kg. per sq. cm., was found to be 0.57 per cent. This, however, does not represent a 50 per cent deterioration,

since the original tensile strength was lower than that obtained with the compounds containing sulfur as a vulcanizing agent. The quantity of oxygen found to be equivalent to a 50 per cent deterioration in tensile strength was 0.72 per cent.

On the basis of results obtained with properly cured and overcured compounds vulcanized with sulfur, it is possible that the quantity of oxygen equivalent to a 50 per cent deterioration in this case might have been higher for the compound at technical cure. On the other hand, the tetramethylthiuram disulfide type of cure may produce a vulcanizate which requires less oxygen for a given physical deterioration than is necessary in the case of the sulfur-di-o-tolylguanidine compound. Additional work is required to clear this point.

SUMMARY AND CONCLUSIONS

1. A previous investigation of the rate of oxidation of rubber over the temperature range of 60° to 80° C. has been extended to 90°, 100° and 110° C.

2. The rate of oxidation over the range which accounts for substantial deterioration of tensile strength appears to be a straight-line function of the time of aging from 60° up to an including 90° C. The rate of oxidation at 100° C. appears to diverge somewhat from a straight-line function of time decreasing as oxidation proceeds.

3. The rate of oxidation increases with increased temperature. Over the range of 60° to 110° C., the rate is doubled for each 7.5° increase in temperature, corresponding to a temperature coefficient of oxidation of 2.5.

4. Tensile strength decreases as a straight-line function of the time of aging and of the quantity of oxygen absorbed.

5. The quantity of absorbed oxygen, determined by weight gain corresponding to a 50 per cent decrease in tensile strength, varies with the temperature of oxidation. At 60° C. the oxygen requirement for 50 per cent deterioration is about 1.30 per cent, and at 110° C. about 0.65 per cent on the rubber hydrocarbon content.

6. Tensile strength increases, probably due to a mild curing effect, when specimens of the compound are heated in an atmosphere where the oxygen is replaced with carbon dioxide for the same periods of time at 80° and 110° C., were required to cause a 50 per cent deterioration in tensile strength in an oxygen atmosphere.

7. With increased time of vulcanization, the rate of oxidation increases. Oxidation appears to be autocatalytic in the case of overvulcanized rubber.

8. As time of vulcanization increases, there is a decrease in the quantity of oxygen required to cause a given decrease in tensile strength.

9. Thickness variations of 0.43 to 1.90 mm. in test-specimens of a compound containing an antioxidant do not affect quantity of oxygen absorbed or degree of tensile strength deterioration when aging is conducted at 80° C. and 3.5 kg. per sq. cm. oxygen pressure.

10. When tetramethylthiuram disulfide is used for vulcanization in place of sulfur, there appears to be no change in the mechanism of oxidation, but the rate of oxidation is reduced.

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A CRITICAL ANALYSIS OF THE T-50 TEST FOR STATE OF VULCANIZATION *

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In 1938 the rubber industry was the fourteenth largest in the United States, employing approximately 130,000 people. The eminent position which it has assumed dates from the discovery of vulcanization. Before this discovery, rubber was of comparatively little commercial importance. For one hundred years the principles and basic technique of vulcanization have not changed. Today, as one hundred years ago, rubber is transformed to its most useful state by the addition of sulfur and the application of heat. It may safely be said that vulcanization is the foundation of the modern rubber industry. Consequently its technical application and control are of vital importance.

STATE OF CURE

In formulating a rubber compound for a specific purpose, those ingredients are chosen which will give the desired properties in the finished product. The compound then is vulcanized in order to develop those properties to their maximum extent.

Vulcanization is progressive and may be carried to any desired state by controlling the time and temperature at which it is effected. For any rubber stock, compounded for specific properties, there is a state of vulcanization or cure which brings these properties out to their fullest degree. As every rubber technologist knows, no rubber concern can hope to remain long in business without exercising strict control over the state of cure to which it brings its products.

State of cure indicates the position of a cure in a series of progressive cures. It may be represented schematically by Figure 1 as a function of the time of vulcanization carried out at a constant temperature.

As illustrated in Figure 1, the progressive states of cure are: *undercure*; *optimum cure*, as judged by maximum tensile strength after aging; *maximum cure*, as judged by maximum tensile strength before aging; *overcure*; and *reversion*, or extreme overcure.

TESTS FOR STATE OF CURE

With such wide variation in physical properties for different states of cure, it is not surprising that the rubber industry has expended a great deal of effort in developing tests for indicating state of vulcanization.

In various factories and laboratories at one time or another the following tests have been used:

1. Percentage of sulfur combined with rubber.
2. Maximum tensile strength or tensile product.
3. Maximum stress for a given strain or modulus.
4. Optimum resistance to aging.
5. Specific properties for special service requirements: *e. g.*, cold flow, hardness, etc.

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These tests have been of immense value, and every technical man in the rubber industry is familiar with the significance and limitations of each.

In recent years a new method, known as the T-50 test, has been adopted in an increasing number of laboratories for indicating state of cure. Several articles have appeared in the literature, and it is the purpose of this paper to analyze critically the data which have been published and to determine the relative merit of this test in comparison with the older methods. New data have been obtained where it was believed that published data were not sufficient to arrive at a clear conclusion.

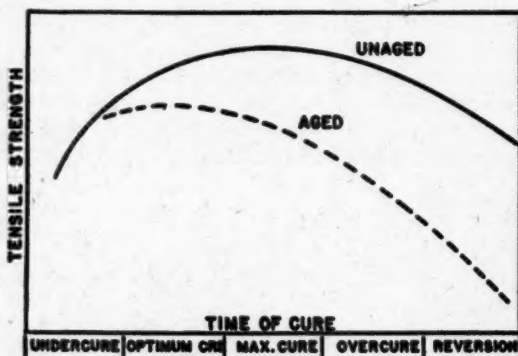


FIG. 1.

THE T-50 TEST

Basically the T-50 is a quantitative measure of the extent of immunity of a rubber compound to the effects of temperature changes. Prior to the discovery of vulcanization the commercial use of rubber was limited because it became brittle at freezing temperatures and soft and tacky at around 100° F.

As has been stated, the discovery of vulcanization was the realization that the addition of sulfur to rubber under the influence of heat greatly decreased its sensitivity to temperature changes. It was only natural that this phenomenon ultimately would be investigated quantitatively. Probably it was not undertaken until recent years because of no easy laboratory method for chilling rubber much below 0° C. until dry ice became readily available.

Gibbons, Gerke and Tingey¹ first announced the T-50 test, and their article gives an excellent account of the fundamental principles which led to its development. They found that unvulcanized rubber, stretched and frozen at a low temperature, would, on gradual heating, retract to 50 per cent of its initial elongation at 18° C. On investigating the behavior of cured rubber under similar conditions, it was discovered that it too would retract to 50 per cent of its initial elongation at some temperature proportionately lower than 18° C., depending on how far vulcanization had progressed.

Based on this principle, a suitable apparatus was designed, and specifications were set up for performing the T-50 test. Acetone was used as a cooling medium and was chilled to -70° C. by circulation through a coil surrounded by dry ice. Stretched samples immersed in the cold acetone bath remained elongated and retracted gradually when the bath was warmed with an electrical immersion heater.

The temperature at which the samples had retracted to 50 per cent of their initial elongation was noted and recorded as the T-50 value. It was found that the T-50 temperature became progressively lower with advancing state of cure, being 18° C. for unvulcanized rubber and approximately 13° lower for each per cent of sulfur which had combined with the rubber. Thus for a compound which had 1 per cent combined sulfur, the T-50 would be approximately 18° minus 13°, or 5° C. Likewise, for 2 per cent combined sulfur, the T-50 test would be approximately -8° C.

T-50 AND COMBINED SULFUR

Rubber technologists long have associated percentage combined sulfur with state of cure. Although this method has many shortcomings, it has proved to be a practical criterion, and is preferred in many laboratories. Inasmuch as the percentage combined sulfur increases and T-50 decreases as cure progresses, it is natural to ask if a quantitative relation exists between them.

Gibbons, Gerke, and Tingey¹ found the approximate relation stated in the preceding section. This relation was studied, however, in greater detail by Gibbons, Gerke and Cuthbertson² with the following conclusions:

1. For vulcanizates which contain no zinc oxide, but vary in composition otherwise, there is a definite relation between T-50 and combined sulfur for all compounds.

2. For vulcanizates which contain zinc oxide, but vary in composition otherwise, no general relation exists between T-50 and combined sulfur for all compounds. In this case the relation was found to vary according to the type of acceleration. No better correlation is obtained, even though the combined sulfur data be corrected for that portion of the sulfur which combined with the zinc as zinc sulfide.

3. For vulcanizates which contain zinc oxide, a definite relation exists between T-50 and combined sulfur for each compound.

Although the reference² cited above is an excellent piece of work, it left some questions unanswered which are believed essential for the present analysis.

Consequently a series of compounds were mixed (see Table I) in which the acceleration was varied to include one of each type in common use: namely, a thiazole, an aldehyde amine, a guanidine and a thiuram. This series was as follows:

TABLE I

Recipe	Parts by weight			
	A	B	C	D
Smoked sheet	100	100	100	100
Zinc oxide	10	10	10	10
Stearic acid	2	2	2	2
Sulfur	3	3	3	3
Zinc salt of mercaptobenzothiazole	1	—	—	—
Butyraldehydeaniline condensate	—	1	—	—
Diphenylguanidine	—	—	1	—
Tetramethylthiuram monosulfide	—	—	—	0.2

Samples were cured in a press over a range of time at 30 pounds' steam pressure. Several long overcures were included purposely to determine how T-50 values progressed in this respect. T-50 and combined sulfur determinations were made on each sample. Also physical tests were secured with a Scott stress-strain machine, using dumbbell test pieces. The results obtained are tabulated in Table II.

The relation between T-50 and combined sulfur for each of the accelerators studied is brought out clearly in Figure 2.

It is evident that basic types of accelerators, such as a guanidine or an aldehydeamine, give higher T-50 readings for a given amount of combined sulfur

TABLE II

Recipe	Cure (minutes at 274° F.)	Combined sulfur (grams per 100 grams of rubber)	T-50 °C	T-50 °R	500% modulus (lbs. per sq. in.)	700% modulus (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elonga- tion at break (%)
A	5	0.54	10.2	283.2	010	130	590	946
	10	0.95	7.5	280.5	200	530	1650	903
	15	1.19	3.6	276.6	260	1050	2920	903
	30	2.03	- 8.8	264.2	440	2070	3310	810
	45	2.44	-15.0	258.0	540	2120	3320	803
	60	2.65	-20.0	253.0	660	2300	3450	800
	90	2.87	-25.1	247.9	620	2480	2980	753
	120	2.95	-27.1	245.9	560	2050	3120	796
	150	2.96	-29.0	244.0	600	2160	3200	786
	180	2.96	-30.9	242.1	600	2220	2940	763
B	5	0.56	12.4	285.4	050	140	900	1103
	10	1.02	8.6	281.6	270	900	2500	896
	15	1.41	3.9	276.9	430	1790	3620	830
	30	2.21	- 7.8	265.2	900	3320	4200	770
	45	2.49	-12.2	260.8	950	3750	4320	743
	60	2.69	-16.7	256.3	990	3840	4190	723
	90	2.89	-22.0	251.0	980	3700	4080	730
	120	2.92	-23.9	249.1	830	3470	3880	740
	150	2.94	-24.8	248.2	800	3310	3780	720
	180	2.96	-25.5	247.5	730	2910	3530	723
C	5	0.30	15.5	288.5	—	—	50	976
	10	0.54	12.9	285.9	—	130	660	1173
	15	0.70	11.6	284.6	020	220	940	1013
	30	1.04	8.4	281.4	200	690	2090	926
	45	1.34	6.8	279.8	200	940	2380	883
	60	1.54	4.7	277.7	330	1190	2560	856
	90	1.96	- 2.5	270.5	620	2180	3200	783
	120	2.26	- 9.8	263.2	550	2380	3470	790
	150	2.47	-15.8	257.2	860	3060	3600	753
	180	2.64	-18.7	254.3	700	2950	3510	746
D	5	0.73	7.8	280.8	020	150	380	886
	10	1.39	- 1.0	272.0	410	1750	3760	863
	15	1.96	-12.4	260.6	730	2780	4190	793
	30	2.85	-28.5	244.5	750	3040	3980	763
	45	2.87	-31.8	241.2	780	2860	3710	766
	60	2.92	-33.0	240.0	520	2400	3590	786
	90	2.93	-35.5	237.5	680	2120	3300	776
	120	2.92	-36.9	236.1	500	1740	3230	816
	150	2.93	-38.0	235.0	600	1940	2840	770
	180	2.92	-38.9	234.1	480	1830	2970	776

than do acidic types, such as a thiazole or a thiuram. The extent of this variation is indicated in Table III.

For a given amount of combined sulfur, the lowest T-50 value appears to be obtained with a thiuram type of accelerator. This may explain why thiurams are preferred for producing stocks with minimum cold flow characteristics.

Further study of Figure 2 reveals that in prolonged overcures T-50 values continue to become lower, at a decreasing rate, after combined sulfur remains virtually constant. This is in agreement with data reported by Somerville³. It would appear that the T-50 test records the effect of those factors which contribute to vulcanization even after all available sulfur has been consumed. Tuley⁴ has referred to these factors collectively as "vulcanization potential".

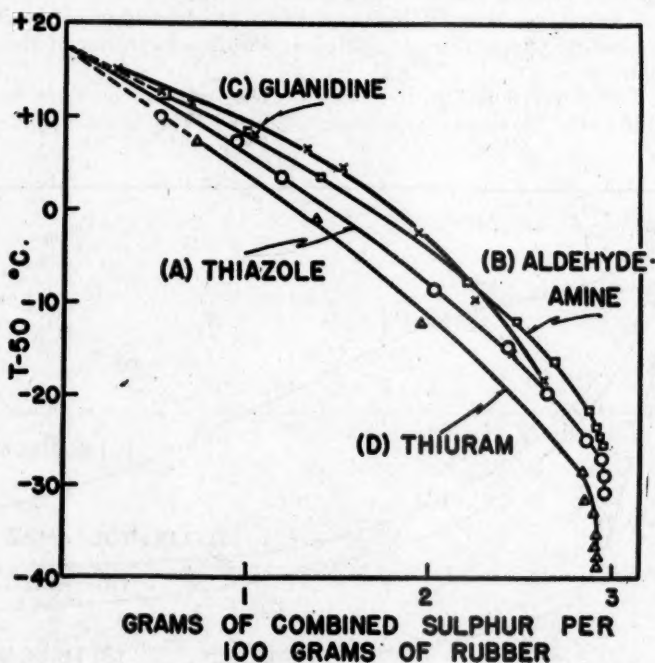


FIG. 2.

TABLE III

T-50 FOR A CONSTANT AMOUNT OF COMBINED SULFUR WITH VARIOUS TYPES OF ACCELERATORS

Parts of sulfur combined with 100 parts of rubber	Guanidine	Aldehydeamine	Thiazole	Thiuram
1	9.3	8.3	5.8	4.0
2	-3.0	-4.6	-8.2	-11.6

The data of Gibbons, Gerke and Cuthbertson and the present study indicate then that no general relation exists between T-50 and combined sulfur. A specific relation, however, exists between these properties for any one compound. For practical purposes, however, it may be stated that the approximate relation of a decrease of 13 degrees in T-50 for each per cent of combined sulfur applies in a very general way within the normal curing range. This is subject, however, to a possible error of from 10 to 40 per cent.

T-50 AND STATE OF CURE

The T-50 test was designed to indicate the relative state of cure of a compound. Figure 3 shows the variation of T-50 with time for cure for compounds A, B, C and D (Table 1).

The curves in Figure 3 are characteristic and bring out the fact that, as the state of cure progresses, T-50 values continue to decrease. The form of these curves suggested plotting the data on logarithmic scales, and a very interesting relation was found, as shown in Figure 4, where the logarithm of the T-50 expressed in absolute temperature is plotted against the logarithm of the time of cure in minutes.

All the T-50 data reported in the literature were plotted, as above, on log-log paper, and the same characteristic relation was found. The data for each accelera-

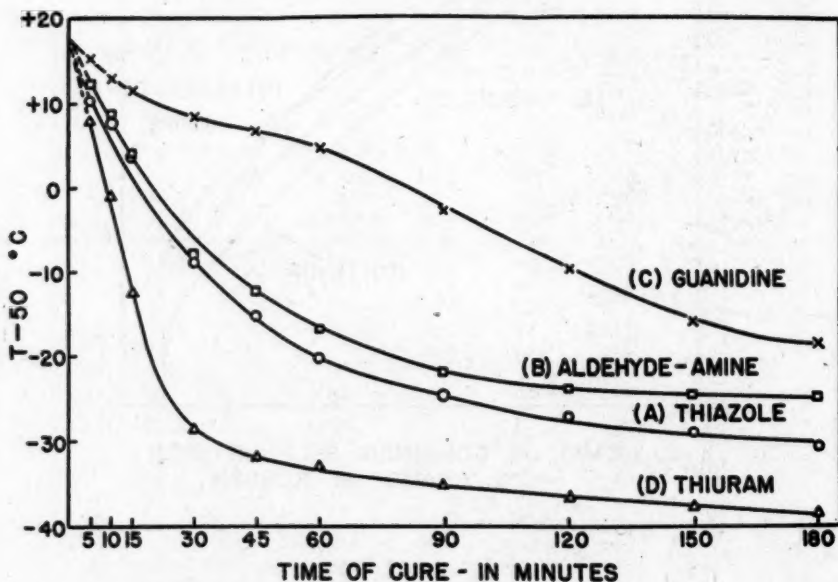


FIG. 3.

tor are seen to fall on three straight lines, which vary in slope. This suggests three distinct stages of vulcanization. When the three portions of the plot are correlated with physical properties, the first portion is seen to correspond with undercures. The second line, of maximum slope, corresponds to those cures which lie within the limits of maximum physical properties. Overcured stocks fall on the third portion of the line. There seems to be evidence that, in some stocks at least, the cure which gives optimum aging occurs at the first break in the line. Perhaps minimum cold flow would be found at the second break.

These observations are represented schematically in Figure 5.

Undercures fall on line AB. Maximum cures fall on line BCD. The highest physical properties frequently fall near point C, which lies about midway between B and D. As stated above, there is some evidence that the cure which gives optimum aging may fall at point B. Overcures fall on line DE.

The curing range of a compound appears to be in proportion to the slope of the second part of the line (BCD). Note the comparison in Figure 4 between

the line for the thiuram-type accelerator, which has a short curing range with normal sulfur, and those for the zinc salt of mercaptobenzothiazole and butyraldehydeaniline, which have long curing ranges.

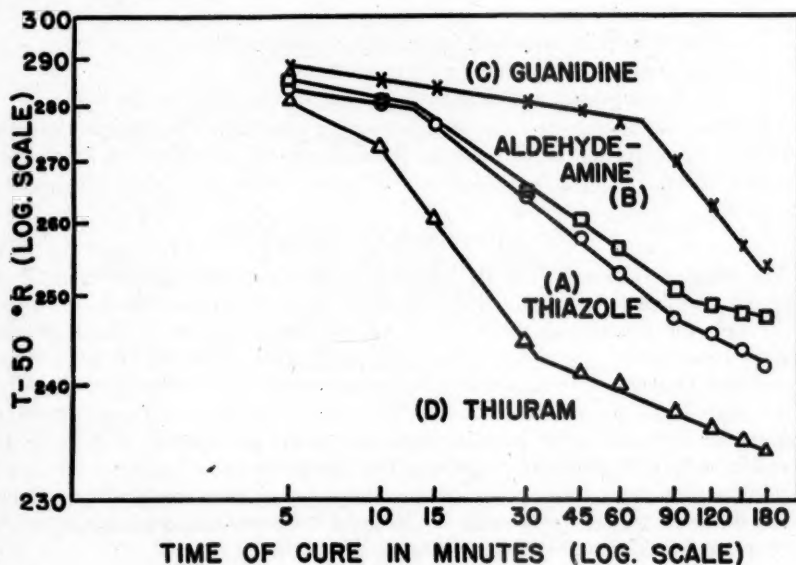


FIG. 4.

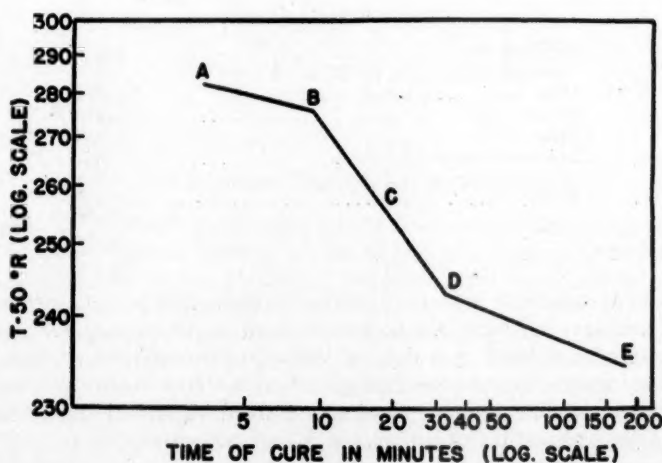


FIG. 5.

It is believed that the above observations should be confirmed on a larger number of stocks. Perhaps the plotting of T-50 data on log-log paper would bring pertinent properties of a compound into sharper focus, which would be of immense practical value. There also appear to be interesting possibilities in

studying these facts in relation to various vulcanization theories. Inasmuch as T-50 decreases with progressive state of cure, it may be considered an index of the extent to which vulcanization has taken place. The relation shown above between T-50 and time of cure may be expressed mathematically as:

$$\log T-50 = K \log t$$

where T-50 is expressed in absolute temperature,
°R., and t is the time of cure in minutes.

K is a constant, which is proportional to the slope of the line.

This equation is characteristic of a first-order reaction. The present data suggest that vulcanization takes place in three stages, all of which are reactions of the first order.

T-50 AND PHYSICAL PROPERTIES

The relation between T-50 and physical properties, *viz.*, tensile strength and modulus, has been studied by Roberts⁵ in an excellent article entitled: "Use of T-50 Test for Evaluating the Rate of Vulcanization of Carbon Black Stocks". He used essentially the same method and apparatus as employed by Gibbons, Gerke and Tingey⁴, although some minor changes and improvements are described.

An analysis of these data shows the T-50 test to be very sensitive in detecting differences between curing rates of different carbon gas blacks. The T-50 data correlate well with physical properties, but are much more sensitive and reproducible within closer limits than are the stress-strain data, as shown by a series of 19 different rubber tests made by Roberts on slow, medium and fast-curing carbon gas black samples in the following test recipe.

TABLE IV
COMPOUND No. 1 (ROBERTS)

Smoked sheet	100
Carbon black	50
Pine tar	3.50
Stearic acid	4.00
Zinc oxide	5.00
Mercaptobenzothiazole	0.75
Antioxidant	1.00
Sulfur	3.00
	<hr/>
	167.25

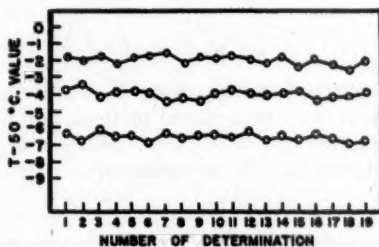
Samples were cured in a press over a range of time at 30 pounds' steam pressure.

T-50 readings and stress-strain curves were made on samples representing the three grades of black each day for 19 days to determine the accuracy of the test. These results are plotted in Figure 6. The T-50 results obtained on the same stock in 19 different tests show only a slight variation; the average variation is of the order of 0.4 to 0.5° C.

In Figure 7 the modulus values obtained from the same samples are plotted, and it is evident that considerable variation was obtained, although the author states this variation can be classified as within experimental error.

A comparison of these graphs would indicate that T-50 data are more sensitive than modulus data for judging state of cure. The data also indicate that T-50 data are reproducible within small limits of experimental error, *i. e.*, 0.5°.

Roberts concluded that, "The use of the T-50 test is an excellent method for evaluating the effect on rate of vulcanization of carbon gas blacks. The test has proved to be a rapid and accurate means for measuring this value from the standpoint of production control."



Top line—Slow rate of vulcanization.
Center line—Medium rate of vulcanization.
Third line—Fast rate of vulcanization.
Compound No. 1 vulcanization 60 min. at 30 lbs.

Fig. 6 (From Roberts).

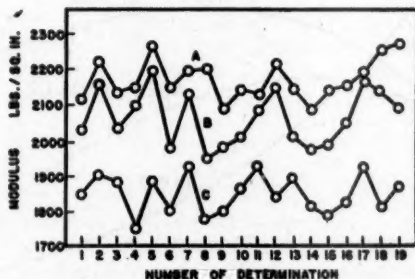


Fig. 7.

T-50 IN PRACTICAL COMPOUNDING

The use of the T-50 test in practical rubber compounding has been well treated by Tuley⁴. He describes a suitable apparatus and technique, and then illustrates practical uses of the test for comparing anti-scorch materials; degree of activation or retardation by antioxidants; coordination of cure; state of cure in low sulfur compounds, reclaim compounds and latex compounds; control testing; material uniformity; and determination of reversion. The practical aspects of the test are illustrated by data from stocks representative of commercial practice.

The work of Roberts⁵ in evaluating the rate of vulcanization of carbon blacks was treated in a former section, and is an example of a practical application of the T-50 test.

Haslam and Klamann⁶ made a thorough study of the T-50 test applied to zinc oxide compounds. In investigating the technique of performing the test, they found no difference in T-50 data if the initial temperature of the bath were -50°C . instead of -70°C . as suggested by the originators of the test¹. They also found no difference in T-50 values of identical samples tested daily for a period of one to 14 days after vulcanization. After these fundamentals were established, the

curing rates of various zinc oxides were studied, and results expressed as the minutes of cure required at a given temperature to reach a T-50 value of -7°C . It was concluded that the T-50 test was an efficient reliable method for determining the state of cure of a rubber compound. They state, however, that T-50 data did not reveal any basic information which could not be determined by conventional methods.

UTILITY OF THE T-50 TEST

All the published data on the T-50 test have been examined, and the test has been compared with each of the conventional methods for judging state of cure. In determining the acceptability of a test, ease of manipulation and reproducibility of results must be considered, as well as significance of the data obtained. In-

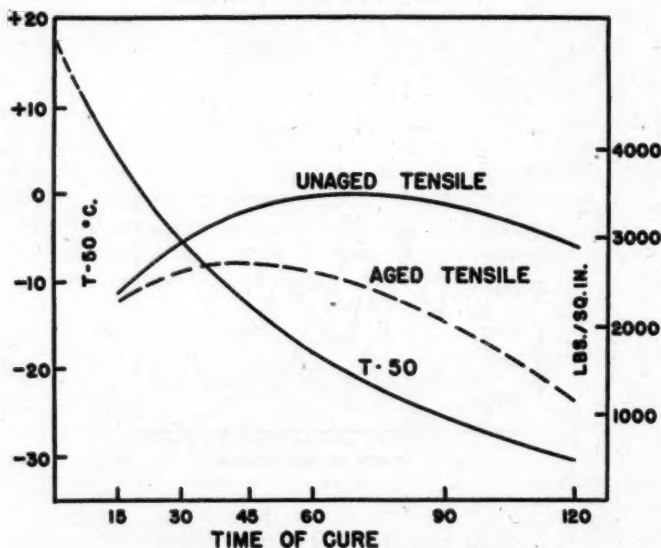


Fig. 8.

vestigators who have reported on the T-50 test in the literature have satisfied themselves that the test is easy and quick to perform, and they have found it possible to reproduce results within narrow limits of experimental error^{4, 5, 6}. It would appear, then, that the T-50 test satisfies the prerequisites of ease of manipulation and reproducibility of results.

In comparison with stress-strain data for indicating state of cure, it would seem safe to conclude that the T-50 test, although probably no easier to perform, is more sensitive and consistent, as shown by Roberts.

Tuley⁴ calls attention to the high tensile strengths often obtained on latex films, even if the compound is undercured. Such data might lead one to believe that the stock was cured to its optimum, but aging nevertheless would be comparatively poor. The T-50 test presumably would detect such a defect once the optimum conditions were established.

In comparison with analyses for combined sulfur, the T-50 test obviously is much quicker and would seem to be at least as sensitive for following the rate

of cure. In fact, it has been shown in the present study and by Somerville³ that T-50 continues to decrease in overcures after combined sulfur determinations reach a constant value. This would indicate that T-50 data are more sensitive for following cure over a broader range.

For practical purposes T-50 data are of comparative rather than absolute value. A T-50 value by itself means very little unless it be referred to other physical or chemical properties of a rubber compound, which vary with state of cure. As an illustration of this principle, tensile strength, aging and T-50 data for a rubber compound are projected on Figure 8, showing how they vary with progressive states of cure.

T-50 data appear to be of most value as a reference point which ties in various properties with state of cure. Having determined for any given compound that state of cure which brings out the desired properties to their fullest extent, the T-50 value is noted and the maximum development of those properties is insured in subsequent batches by curing to the same T-50.

Generally speaking, T-50 cannot be used universally to predict tensile strength or percentage of sulfur combined with the rubber except for a specific compound where the relation has been established. One exception cited in the literature² is the case of compounds containing no zinc oxide, where there appears to be a definite relation between T-50 and percentage of combined sulfur. This type of compound, however, is of limited commercial importance at the present time.

The observation made in a former section of this paper of the characteristic relation which results when T-50 and time of cure are plotted on log-log paper may be the basis for considering T-50 data of absolute as well as comparative value. This relation must be studied in greater detail, however, before any important conclusions can be drawn.

CONCLUSIONS

It is the consensus of opinion in the literature that the T-50 test is reliable, sensitive and easy to perform. The present analysis of the T-50 test, compared with other methods for determining state of cure, indicates it to be more sensitive and consistent than stress-strain data and easier to perform than sulfur analyses. In addition it seems to be a more constant function of state of cure than combined sulfur, and detects other factors contributing to state of cure which, for convenience and lack of a true understanding of their exact nature, may be referred to collectively as "vulcanization potential".

Plotting the logarithm of T-50, expressed as absolute temperature, against the logarithm of the time of cure seems to hold interesting possibilities for future study.

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DETERMINATION OF THE WATER ABSORPTION OF CRUDE RUBBER AND OF VULCANIZED RUBBER *

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INTRODUCTION

A short time ago the present writer published an article¹ on "Purified Rubber", which constitutes a detailed introduction to the present study. In this earlier article, the ever-growing interest in the production and use of purified rubber was pointed out. Further studies of various methods of purification and the testing of industrial samples made clear the necessity of having at one's disposal some standard method of determination for use in studying the water absorption properties of rubber.

In other words, we have tried to find an effective method of testing crude rubber from the view-point of its suitability as a basic material for the manufacture of vulcanized rubber with low water absorption. This task is therefore quite different, for example, from a laboratory determination of the water absorption of rubber steam hose. We propose to test the basic material with a view to its suitability in numerous unknown vulcanized products, whereas in the case of the laboratory it is merely a question of forming an estimate of the final product as such, under conditions which approach those under which the rubber is to be used.

This involves also the possibility of using purified rubber in unvulcanized form, so that the water absorption properties of the crude product as such must also be determined. We have known all along from the literature², and have verified by our own observations, that the water absorption of vulcanized rubber is not always proportional to that of crude rubber. It was therefore necessary to investigate rubber both in the crude and vulcanized state.

Current literature indicates that various laboratories use widely different methods for determining water absorption. Rubber factories, too, have their own methods, as is evident from information received on the subject. Naturally it has been our purpose to carry out our determination in such a way as to ensure a result of maximum value to consumers of purified rubber. In the following pages we shall give a detailed description of the development of our test method and of the determination itself. Any criticism from rubber manufacturers will be most welcome, since we shall be glad to replace our test method by another if it should appear that consumers of purified rubber attach greater value to results obtained by other methods.

In view of the diversity of methods for determining the water absorption of rubber, the question arises how far the results are directly comparable by the use of computation factors. Within certain limits, so far as the conditions under which the determination takes place are concerned, such a comparison is possible thanks to the formulas of Taylor and Kemp³, the most important of which will be cited below.

* Translated by A. H. Krappe for RUBBER CHEMISTRY AND TECHNOLOGY from the *Archief voor de Rubbercultuur*, Vol. 28, No. 3, pages 176-188, 1939.

INFLUENCE OF CONDITIONS IN THE DETERMINATION OF WATER ABSORPTION

In the following pages we shall not go into the derivation of formulas; suffice it to say that an exact mathematical treatment of the water absorption of rubber does not in general appear possible and that the formulas cited below are largely empirical. Some rubbers are said to behave differently from what might be expected on the basis of the formulas. We give below the most important factors which influence the results of the determinations.

SIZE AND FORM OF THE SAMPLE

Satake⁴ pointed out that water absorption at the beginning is strictly proportional to the surface exposed to water or water vapor. For this reason water absorption is expressed, for example, in milligrams per unit of surface, and the results therefore are independent of the size and form of the sample.

If the results are expressed in milligrams per unit weight, they are independent only of the size of the sample if it approaches the form of a fleece, in other words, if the lateral surface can be neglected in comparison with the total surface.

IN WATER OR WATER VAPOR

From the work of Lowry and Kohman⁵ it is evident that the same water absorption is obtained by immersion of a sample in water as by allowing it to stand in an atmosphere saturated with water vapor in equilibrium with water at the same temperature. Observations in the older literature, at variance with this result are the results of experiments made without special precautions, and must be explained by the fact that the water and water vapor were not in equilibrium. Even a small deviation from the state of equilibrium has a very great influence on water absorption.

TIME

Taylor and Kemp found that, in general, weight increase by absorption takes the form of a parabola. By considering, then, the logarithm of the weight increase of the sample as a function of the logarithm of the time, we obtained a straight line expressed by the equation:

$$\log c = n (\log t - \log t_1) + \log c_1,$$

where

$$\begin{aligned} c &= \text{weight increase in time } t \\ c_1 &= \text{weight increase in time } t_1 \text{ found by experiment} \\ n &= \text{constant} \end{aligned}$$

If the water absorption takes place in water-saturated air or in water, the experimental value of n appears to be 0.50.

The equation may then be written as follows:

$$c = c_1 \sqrt{\frac{t}{t_1}} \quad (1)$$

VAPOR PRESSURE

If absorption takes place in water or in a water-saturated atmosphere, then:

$$c = c_1 \sqrt{\frac{tp}{t_1 p_1}} \quad (2)$$

If a weight increase c_1 is measured after a lapse of time t_1 in a saturated vapor tension p_1 , the weight increase c after a lapse of time t in a saturated vapor tension p may be calculated.

TEMPERATURE

If absorption takes place in water or saturated water vapor, the influence of the temperature may be calculated by substitution in Equation (2) of the vapor pressures (recorded in the literature) at the temperatures in question.

ABSORPTION IN ACID SOLUTIONS

Absorption in acid solutions may also be computed from Equation (2) by substitution of the vapor pressure of the acid solution in question.

From the data of Boggs and Blake⁶ it is known that the surface tension of the solution is also of influence if the absorption determination takes place in a fluid. If therefore the acid solutions contain capillary-active components, Equation (2) must not be applied.

EXPERIMENTAL PART

SAMPLES

To make possible a correct comparison of the water absorption of crude rubber with that of vulcanized rubber, samples of the same form were selected before both determinations. For vulcanized rubber it was most simple to use the same form of samples which had been employed by us in our inquiry into vulcanization, *viz.*, circular disks about five millimeters thick and 45 millimeters in diameter. After choosing the form of the samples, the problem how to prepare these samples from crude rubber still remained. Preliminary experiments showed that the best results could be obtained by pressing the required number of plies of crepe rubber under a pressure of 3000 lbs. per sq. in. for 20 minutes at 90° C. For this purpose a Carver laboratory press with electrically heated plates was used. In this way fairly transparent slices were obtained, from which, by means of a Schopper punching machine, the desired disks were secured. If the crude rubber to be tested is abnormally plastic, a change in temperature during pressing may cause the rubber to be compressed excessively (usually with the formation of air bubbles), or may result in the plies of crepe not being sufficiently compressed, as indicated by the production of a non-transparent rubber sheet.

Before adopting this method, we carried out a test in which the rubber was somewhat plasticized on a mill and then was pressed while hot, and a second test in which the rubber was further plasticized and pressed without heating. The samples thus obtained became sticky during the determination of water absorption, and this constitutes a practical difficulty which is equally undesirable from the theoretical point of view. This stickiness always indicates oxidation processes which are likely to affect water absorption.

IN WATER OR WATER VAPOR

In view of the difficulty of making sure that the water vapor atmosphere was really in equilibrium, it was decided to determine the absorption in water in all cases.

SELECTION OF THE COMPOSITION OF THE VULCANIZATE AND THE VULCANIZATION TIME

In the choice of composition of the rubber mixture to be vulcanized it is necessary to bear in mind that it was not our purpose to obtain a vulcanizate with a minimum water absorption but to work with a type of vulcanizate in which the differences between various rubbers would be as clear as possible. The compound could therefore be of simple composition and need not contain fillers.

Since the water absorption of rubber is accompanied by a corresponding increase in volume, water absorption depends on the resistance of the rubber to volume change. Vulcanizates from the same rubber but with different mechanical properties will thus show differences in water absorption, the stiffer the rubber the lower the water absorption.

Accordingly the mechanical properties of rubber influence its water absorption. It is difficult to determine, however, whether hardness, stiffness or tensile strength is the decisive factor. Furthermore, water absorption depends also on chemical changes during vulcanization, *i. e.*, on the destruction of the proteins and of the sulfur bond. These two influences, one chemical, the other mechanico-physical, act simultaneously and inasmuch as both depend on the vulcanization time, they are not independent of one another. The phenomenon is even more complex since, especially in overvulcanized rubber, oxidation and aging phenomena occur during measurement of the water absorption.

TABLE I
CRUDE RUBBERS.

No.	Ash (%)	N (%)	Preparation
A4347.....	0.19	0.45	Unpurified standard crepe.
A4438.....	0.09	0.25	Purified by repeated creaming.
A4403.....	0.07	0.20	Purified by repeated creaming.
A4421.....	0.09	0.07	Purified by alkali treatment.
A4507a.....	0.23	0.50	Unpurified standard crepe.
A4507b.....	0.11	0.09	Purified by alkali treatment.
A4870.....	0.07	0.10	Purified by repeated centrifuging.

With regard to the problem of comparing the water absorption of different types of purified rubber, in which case it must be borne in mind that the rates of vulcanization of the rubbers may differ widely, it is not sufficient to compare products vulcanized for equal lengths of time. Such a comparison should be made only if it is known that the water absorption is independent of the vulcanization time. If such is not the case, the water absorption, for example, of vulcanization products, must be compared with the optimum mechanical properties or with a like stiffness.

In connection with what has been discussed above, the water absorptions of ordinary rubber and of some purified rubbers were examined to determine the relations between water absorption, composition and state of vulcanization.

Table I gives the data for all the crude rubbers used in the following experiments.

Table II gives the various compositions, and Table III is a survey of water absorption and the mechanical properties of a normal and a purified rubber, both unvulcanized and vulcanized for increasing times. Four different mixtures are included.

A closer examination of the results in Table III shows that purified rubber was poorly vulcanized in three mixtures and that only in the mixture accelerated by mercaptobenzothiazole did it behave like normal rubber.^{*} This is probably due to the quantity of stearic acid contained in the mixture containing mercaptobenzothiazole.

In spite of the fact that the mechanical properties of the vulcanizates obtained with mercaptobenzothiazole as accelerator are only slightly modified by changing the time of vulcanization, the water absorption is considerably affected. The mercaptobenzothiazole vulcanizate should therefore preferably not be chosen for studying water absorption. The fact, too, that the vulcanization temperature is lower than that commonly used in practice and that the addition of stearic acid in the manufacture of articles with low water absorption should be avoided as much as possible, makes this particular mixture appear less suitable.

TABLE II
MIXTURES VULCANIZED

Compound	1	2	3	4
Rubber	92.5	100	100	100
Sulfur	7.5	3.5	2.5	5
Zinc oxide	—	6	0.5	3
Stearic acid	—	0.5	—	—
Mercaptobenzothiazole	—	0.5	—	—
Vulcacit P Extra N	—	—	0.5	—
Diphenylguanidine	—	—	—	1
Temperature of vulcanization.....	148° C.	127° C.	110° C.	147° C.

TABLE III
ABSORPTION OF WATER AT 80° C. AND MECHANICAL PROPERTIES

Compound	Time of vulcanization (min.)	Water absorption (mg. per 100 sq. cm.)				Tensile strength		Elongation at break	
		A4347		A4438		A4347	A4438	A4347	A4438
		7 hrs.	24 hrs.	7 hrs.	24 hrs.				
1.....	90	149	328	81	166	100	58	985	941
	110	145	313	81	161	127	72	990	954
	130	142	301	79	164	142	83	992	966
	150	146	298	79	163	157	144	892	911
2.....	60	132	255	62	120	169	164	823	858
	80	113	247	54	112	169	169	813	864
	100	109	237	52	108	174	156	820	850
	120	122	235	63	120	172	164	815	858
3.....	15	154	313	63	115	127	64	930	817
	30	150	311	63	116	146	143	962	920
	45	150	301	65	120	133	67	979	821
4.....	15	138	238	67	100	158	130	857	872
	30	96	197	51	91	189	118	723	718
	45	90	202	49	107	175	110	659	670
Crude rubber		243	537	95	196	—	—	—	—

Although the water absorption values of the vulcanizates of Mixture 3 are, in spite of the great differences in mechanical properties, little affected by the time of vulcanization, this compound is not suitable as a test mixture for water absorption because the temperature of vulcanization is lower (at higher temperatures, the times are too short) than that commonly used in practice.

Finally with Mixture 4, the influence of the time of vulcanization on water absorption is excessive.

As the composition for studying water absorption, we therefore choose Mixture 1, although even this choice has disadvantages. Table III shows that the influence of the time of vulcanization on the water absorption of purified rubber in this mixture is very small. In other types of purified rubber this influence may

be somewhat greater, as may be seen in Table IV, where the results obtained from a rubber purified by centrifuging (A4870) are included.

In spite of the great influence of the time of vulcanization on the mechanical properties of the vulcanizates of Mixture 1, the effect on water absorption appears to be limited to about 10 per cent. For the determination of water absorption of vulcanized rubber it seemed advisable to choose Mixture 1 vulcanized for 100 minutes at 148° C.

TABLE IV

ABSORPTION OF WATER AT 80° C. AND MECHANICAL PROPERTIES OF MIXTURE 1

Time of vulcanization (min.)	Absorption (mg. per 100 sq. cm.)		Tensile strength	Elongation at break	H
	7 hrs.	24 hrs.			
A4870	93	162	—	—	—
80	71	124	51	1014	32
100	60	114	86	1025	33
120	55	112	124	998	36
150	62	108	150	959	39

CHOICE OF TEMPERATURE

If the determination is carried out in water at 40° C. it is necessary to continue the test for three days before enough water has been absorbed to make possible an exact determination. By raising the temperature, the water absorption is accelerated; but in doing this one runs a risk of oxidation and stickiness, especially in the case of unvulcanized rubber.

TABLE V

ABSORPTION OF WATER AT VARIOUS TEMPERATURES

Rubber	State		Absorption (mg. per 100 sq. cm.)		
			3 days 40° C.	7 hrs. 80° C.	2 hrs. 100° C.
A4347	Crude rubber	Experimental	277	243	140
		Computed	—	220	171
A4403		Experimental	88	78	74
		Computed	—	70	54
A4421		Experimental	68	55	48
		Computed	—	54	42
A4507a	Vulcanized rubber	Experimental	170	158	141
		Computed	—	135	105
A4507b		Experimental	63	58	49
		Computed	—	50	39

The results obtained at higher temperatures may be checked by means of Formula (2), to determine how far they have been affected by the sources of errors just cited.

Table V gives the results of water absorption determinations at 40° C., 80° C. and 100° C. The results obtained at 40° C. were considered to be the most reliable, therefore we have computed by means of Formula (2) the results theoretically to be expected at the higher temperatures. Table V shows that at 80° C. higher values were always obtained experimentally than were expected theoretically, the difference being greatest in the case of unpurified rubber. The de-

termination at 80° C. is however still sufficiently reliable for our purpose. At 100° C. the values found experimentally deviate too much from the computed values, and it did not seem advisable, for our purpose, to carry out the determination at 100° C.

However, for articles used with water or steam at 100° C. or higher, it appears logical to determine water absorption at 100° C.

DURATION OF THE WATER ABSORPTION DETERMINATION

Although after seven hours at 80° C. results were obtained that were in satisfactory agreement with those obtained at 40° C., it was expected that after longer immersion in water at 80° C. oxidation phenomena would occur which would lead to ever increasing errors. Since, however, it was desirable to determine water absorption not only after a definite time, but to find out for how long water absorption followed a normal course, it was important to know the trend of the increase in water absorbed at 80° C. over a period of time, and to compare the results with Formula (1).

TABLE VI
PROGRESS OF THE ABSORPTION OF WATER AT 80° C.

State	Time (hours)	Absorption (mg. per 100 sq. cm.)			
		Rubber A4507a		Rubber A4507b	
		Experiment	Computed	Experiment	Computed
Crude rubber .	7	242	—	54	—
	24	500	450	102	101
	48	747	635	145	142
	72	927	778	173	174
Vulcanized rubber	7	158	—	58	—
	24	315	292	112	107
	48	461	413	172	152
	72	590	507	199	187
	96	715	585	240	215

Table VI gives results for both unvulcanized and vulcanized rubber immersed in water at 80° C. for increasing periods of time. From these figures it will be seen that, starting with the values obtained after seven hours, satisfactory agreement between the values found experimentally and the computed ones still exists after 24 hours. After longer immersion in water at 80° C. increasing deviations occur, and these were greater with normal rubber than with purified rubber.

To determine whether the course of water absorption was normal, it was decided in the standard test method always to determine water absorption in water at 80° C. after 7 and after 24 hours.

THE METHOD OF DETERMINING WATER ABSORPTION

For the sake of clarity, the method of determination of water absorption tentatively accepted as standard will be summarized.

CRUDE RUBBER

A test sheet is compressed for 20 minutes at 90° C. under 3000 lbs. per sq. inch in a Carver laboratory press. This sheet must be entirely transparent and must not contain air bubbles. In the case of abnormally hard or soft rubbers this

can be obtained only by using higher or lower temperatures, the time and pressure remaining the same. After these sheets have stood for one night, three disks are died out with a Schopper punching machine, with diameter of 45 millimeters. The disks are weighed before immersion and again after 7 and 24 hours in distilled water of 80° C. After the first measurement the water is renewed. The weight increase is expressed in milligrams per 100 sq. cm., computed to the original surface. The determination is carried out in triplicate.

VULCANIZED RUBBER

A mixture of 92.5 parts of rubber and 7.5 parts of sulfur in the form of a sheet 5 millimeters thick is vulcanized for 100 minutes at 148° C. Disks are punched from this sheet as before, and the water absorption is determined in the same manner as for crude rubber.

SUMMARY

In the introduction the purpose of the investigation is described which is the development of a method suitable for the determination of the water absorption of crude and vulcanized rubber, and which, in conjunction with ash and nitrogen determinations is especially adapted to the testing of purified rubber.

The conditions which affect the results of water determinations are reviewed, with special reference to the formulas of Taylor and Kemp, which make it possible, within certain limits, to compare results obtained by different determination methods.

The reasons for selecting the foregoing method of determination of water absorption are described. It is pointed out that water absorption depends to different degrees on the time of vulcanization. In the rubber-sulfur mixture which was chosen, the influence of the degree of vulcanization is small, so that it is sufficient to vulcanize all types of rubber for the same length of time. At the same time it is shown that the results obtained by immersion of rubber for 7 and 25 hours at 80° C. still sufficiently agree with the values computed from the formulas of Taylor and Kemp.

A method of measuring water absorption is described in detail. The question arises to what extent rubber manufacturers may use this method, in conjunction with ash and nitrogen determinations, method for estimating the quality of purified rubber.

Rubber manufacturers are urged to give their opinion of this proposed method. Some other method will be considered if it should appear that manufacturers prefer this other method.

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THE CREAMING OF RUBBER LATEX *

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Among methods of concentrating rubber latex, the creaming process has, quite independently of the evaporation and centrifuge processes, aroused increasing interest because of its special technical features. The tendency of the rubber particles in latex to cream as a result of the difference in specific gravity of the rubber and serum is a phenomenon which has been known for a long time. Hancock himself observed that when latex is stored, displacements in the concentration take place and he proposed to utilize this phenomenon in the preparation of very pure rubber particularly free of colored impurities.

In 1824 Hancock suggested that rubber latex be diluted with water to one-fourth its concentration and the serum removed after a short period of standing. By repeating this process several times, a particularly pure product was said to result. In 1826 Faraday too described the same process.

However, the displacements in concentration which become evident in latices which have stood for a long time without the addition of any creaming agent do not lead to any clearly defined layers. The first important observation on the spontaneous separation of two phases in latex by the addition of definite substances was by Traube. Among the substances described by Traube were colloidal mucilages such as gum tragacanth, soluble extract of Irish moss, etc.

Later it was discovered that the creaming of latex can be accelerated not only by these organic colloids but also by solutions of alkalies and even by inorganic salt solutions. The high concentrations of alkalies and salts necessary to bring about this creaming change considerably the difference in specific gravity between the rubber particles and serum and thereby increase the tendency of the latex particles to migrate upwards because of their lower specific gravity with respect to that of the dispersion medium. On account of the high concentrations of the inorganic substances, which are difficult to remove afterward, this method of creaming is of relatively little interest economically at the present time.

During the last ten years great advances have been made in creaming latex by mucilages, both with respect to the technique of the process and chemical treatment of the latex previous to and during creaming. In the present discussion these special technical problems will not be considered in detail; instead the paper will be concerned primarily with the minimum amounts of dissolved organic colloids which bring about creaming and the relations between the nature of these substances and the intensity of their effects.

Among the natural vegetable colloids which are already known to be creaming agents, gum arabic, pectin, gum tragacanth, karaya gum and alginates are particularly worthy of note. In addition to these substances, which have long been known to be creaming agents, an extensive series of vegetable extracts which behave in the same way have been examined in the last few years, including extracts of carrageen, cetraria islandica, amorphophallus, various legumes and other substances of similar nature.

All these substances have one property in common, i. e., they are water-soluble vegetable colloids, probably with very high molecular weights. On account of

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the immense wealth of such substances occurring in nature, the number can doubtless be extended indefinitely. During the last ten years a long series of such products have been the object of extensive investigations, and today it is known that, as far as chemical constitution is concerned, they do not consist of individual molecules of the same kind, as it is customary to regard definite organic substances such as isoprene or naphthalene, but on the contrary are mixtures of different high molecular substances having the same fundamental constitution, but of different molecular sizes, *i. e.*, different chain lengths. Each of the names by which the substances mentioned above, *e. g.*, pectin and alginate, is known is therefore only a collective name for an immense number of what have been called by Staudinger polymeric-homologous compounds of which the particular substance *in toto* is composed.

To make this clearer, it seems well to explain once more, if only in a brief way, the concept of polymeric-homologous compounds¹. When an organic hydrocarbon of simple constitution, which possesses a chemical double bond capable of reacting polymerically, undergoes polymerization, a more or less large number of the original molecules, which may reach thousands (depending on the conditions), join to form long chains. Polymerizates can form wherein 10, 50, 100 and 1000 or more, for example, of such base molecules unite. Mixtures of products which are formed by union of base molecules of the same kind, but which differ in the degree of polymerization, are designated as polymeric-homologous substances.

In addition to these series of polymeric-homologous substances, which are built up synthetically from monomers from the base molecules by polymerization to different degrees, polymeric-homologous series can, conversely, be formed by decomposition to different extents of substances, usually with high molecular weights, which are formed in nature. Individual members of a polymeric-homologous series which have the same chemical properties can be distinguished clearly by their physical properties. The most outstanding of the physical properties of mixtures of these high-molecular substances is the viscosity of their solutions. Even at very low concentrations, the viscosities are surprisingly high.

Knowledge of the existence and of the properties of these series of substances makes possible an understanding of the behavior of such substances in the creaming of latex. Perhaps it will also serve to explain the extremely variable and naturally troublesome behavior of a substance which has commonly been assumed in the past to be one and the same creaming agent. In an address on April 12, 1937, before the London section of the Institution of the Rubber Industry, Baker² said that:

"Considerable difficulty was experienced by estates in the early days of the development of the creaming process, owing to variability of the creaming agent. This is well illustrated by the results of the examination at the Imperial Institute of 25 samples of gum tragacanth obtained from different sources, the examination being made by the method recommended by Bishop and Fullerton (*loc. cit.*). Four of the samples gave a cream below 50 per cent, eleven between 50 and 60 per cent, and the remaining ten gave over 60 per cent of dry rubber in the cream. Roughly one-third were definitely unsatisfactory, giving creams containing less than 55 per cent of dry rubber."

These observations, which had previously been made by Bishop and Fullerton, on the variable behavior of gum tragacanth and karaya gum are probably true of all natural substances of similar nature, *i. e.*, in all cases the viscosities of their solutions depend on the extent to which they have been degraded by previous treatment; and their viscous solutions differ in turn in their power of accelerating creaming.

With respect to this last phenomenon, it was of particular interest to study in a systematic way the differences in accelerating powers of a polymeric-homologous series of this character, *i. e.*, the relation between accelerating power and length of chain of the creaming agent. A particularly excellent series of such substances, comprising a series of salts of polymannuronic acid, was kindly placed at our disposal by Mr. Bonniksen of London. The viscosities of the individual members of this series differed considerably, as is shown by the measurements recorded in Table I. These measurements were made in a Cochiu viscometer, with measuring tube 7 mm. in diameter, distance between marks 500 mm. and temperature 18° C. The values in the table represent the number of seconds of flow by this method.

All the substances in this series were outstanding accelerators of creaming. They differed only in their degree of activity, *i. e.*, the higher the viscosity (the

TABLE I
VISCOSITIES OF SALTS OF POLYMANNUROIC ACID

Sample No.	One per cent solution	Three per cent solution
1	40	360
2	60	665
3	75	1260
4	125	not measurable
5	250	not measurable
6	335	not measurable
7	715	not measurable

TABLE II
CREAMING OF LATEX BY ADDITION OF SOLUTIONS OF DIFFERENT VISCOSITIES

Sample No.	Dry substances in cream	Dry substances in serum
1	58.7	12.3
2	60.7	10.3
3	62.0	10.1
4	63.0	8.9
5	63.0	8.4
6	63.2	8.2
7	63.2	7.7

longer the molecular chain), the greater was the accelerating power. This relation is of great significance and may turn out to be important in attempts later to explain the phenomenon on a theoretical basis.

The dependence of the accelerating power on the viscosity of the creaming agent is manifest with the same quantities and concentrations of the creaming agents, by the quantities of rubber component³ remaining in the serum and consequently in the proportions of dry solids in the creams. Data obtained from the same series of samples as before are summarized in Table II. Here the values represent the percentages of total dry substances in the cream and serum, respectively. To each 100 cc. of 40 per cent latex were added 5 cc. of a 1 per cent solution of salts of polymannuronic acid and the mixtures were allowed to stand for 48 hours at 20° C.

The results obtained when various proportions of the same creaming agent were added are equally instructive. Measurements of a representative series are

given in Table III. The values represent the percentages of dry substances in the cream and serum, respectively. Increasing proportions of a 3 per cent solution of methylcellulose were added to 40 per cent latex and the mixtures were allowed to stand for 48 hours. The viscosity of the methylcellulose in the form of a 1 per cent solution in a Cochi viscometer was 135 seconds at 20° C.

From the photograph reproduced in Figure 1, where the results of increasing quantities of creaming agent are shown from left to right, it is evident, without

TABLE III
CREAMING OF LATEX BY VARIOUS PROPORTIONS OF METHYLCELLULOSE SOLUTION

Methylcellulose solution (Parts of 3% solution per 100 parts of latex)	Dry substances in cream	Dry substances in serum
1	42.8	25.7
2	55.1	19.8
3	59.4	14.2
4	60.4	11.2
5	61.6	6.9
6	61.3	6.4
7	61.8	6.1
8	62.0	6.0

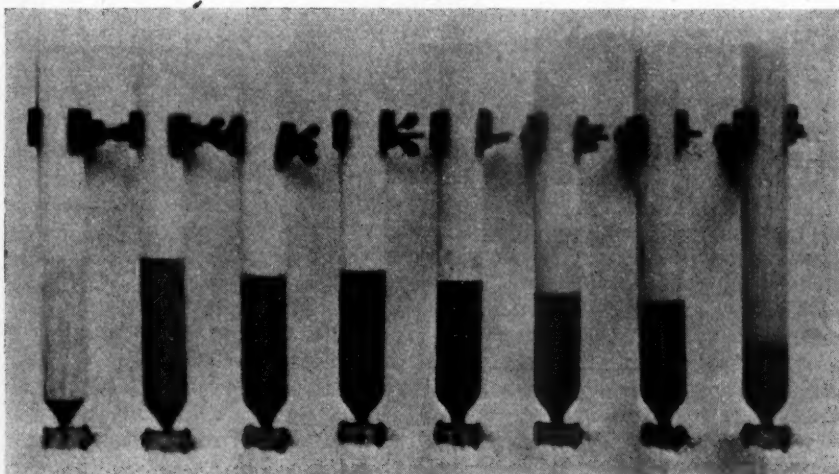


FIG. 1.

further examination of the data, that with relatively small quantities of creaming agent the serum was still milky and therefore still contained considerable quantities of rubber. But above a certain concentration of creaming agent the serum became transparent, and at high concentrations of creaming agent the serum contained practically no rubber. With increase in the quantity of creaming agent, the quantity of serum and the content of total solids in the cream decreased, and the quantity of cream increased until, with further increase in the quantity of creaming agent a point was finally reached where, in virtue of the large quantity of creaming agent, only a very small quantity of serum separated. With a still greater increase in the concentration of creaming agent, the viscosity

of the latex to which it had been added became so great that the latex particles became wholly immobile, and a displacement in the concentration within the liquid was no longer possible. These relations, which were found to be true of the series of salts of polymannuronic acid, probably hold true also of all other similar polymeric-homologous series of the natural products already mentioned above.

Recent progress in the chemistry of high-molecular organic substances has led to a large number of substances having various properties in common with the natural products mentioned. The fundamental properties which are common to all are in fact:

- (1) high molecular weights, *i. e.*, long molecular chains,
- (2) solubility in water.

These new substances can be classified first into those whose fundamental constitutions are formed in nature and which are converted into the most suitable forms only by chemical means, and secondly into those which are synthesized artificially from their elements. To the first group belong all water-soluble derivatives of all the similar natural polymeric carbohydrates already mentioned. Among the water-soluble derivatives, methyl ethers, particularly those of cellulose, are noteworthy. In addition to methyl ethers, ethoxy ethers

TABLE IV

Methylcellulose No.	Viscosity 1 per cent (seconds)	Viscosity 3 per cent (seconds)	Total solids in cream (per cent)	Total solids in serum (per cent)
1	17	55	56.5	15.9
2	20	100	59.0	12.8
3	25	810	60.3	9.7
4	50	2080	61.8	9.5
5	135	3960	63.0	7.7

are particularly interesting, *i. e.*, those compounds which are formed, for example, by the reaction of alkalicelluloses with ethylene oxide, as well as the water-soluble salts of substances of the type of celloglycolic acid. Cellulose xanthate also belongs to this group. All substances belonging to the classes of products mentioned above accelerate the creaming of latex.

A particularly characteristic series of measurements obtained with a series of such substances is shown in Table IV. Here 3 parts of 3 per cent solutions of various methylcelluloses were added to 100 parts of 40 per cent latex. The time of creaming was 48 hours; the temperature was 30° C. The viscosity measurements were made in a Cochius viscometer at 20° C.

As in the experiments with salts of polymannuronic acid, it is evident that for a given quantity and concentration of solution, the higher the viscosity of the methylcellulose solution the greater was the accelerating action of the methylcellulose on the creaming process.

Because of their purity, water-soluble high-molecular products synthesized from their elements are of special interest. In this case also, progress in the chemistry of high-molecular substances has made known a long series of substances, the most interesting of which are, from the present point of view, water-soluble salts of polyacrylic acid. To this same group of substances belong also polyvinyl alcohols and polyethylene oxide.

The fundamentally different chemical constitutions of these substances indicate that their accelerating activities are not attributable to some particular atomic grouping present in all the compounds, but rather that all high-molecular, water-

soluble substances in general have an accelerating action, irrespective of whether they contain an elementary carbohydrate structure or a chain of carbon atoms as their elementary structure, and irrespective of what kind of groups they contain which render them water-soluble, *e. g.*, methoxy, ethoxy, hydroxy, carboxyl or xanthic acid groups.

To be accelerators of creaming, all substances must be soluble and also must be capable of forming molecular dispersions. Substances such as starch, starch dextrin and xylan do not accelerate creaming satisfactorily but their derivatives are good accelerators. In view of this, one is tempted to draw the converse conclusion, *viz.*, that in ordinary starch solutions the starch is not molecularly dispersed.

The results obtained with salts of polyacrylic acid resemble surprisingly those which were obtained with salts of mannuronic acid and with methylcelluloses.

As far as hindrance of Brownian movements and reversible aggregation of latex particles by creaming agents are concerned, Baker² has already described these effects in detail. The observation of Baker that starch which had no accelerating action on creaming did not, at the concentrations used in the creaming experiments, have any retarding effect on the Brownian movement, confirms the view that substances must be dissolved molecularly to be accelerators of creaming.

It is surprising that all substances which are regarded as satisfactory creaming agents are active, even at very low concentrations. With most of these substances, quantities corresponding to 0.05 to 0.1 per cent, based on the quantity of latex, show appreciable accelerating effects. Furthermore, substances which show little or no accelerating activity at these concentrations give good results with respect to rate of separation, quantity of cream and concentration when they are used in higher concentrations. This means that every substance which has the power of accelerating creaming has a maximum effect at some definite concentration which is characteristic of the substance.

It is of general interest that substances which have been described in the present work as creaming agents in the concentration of latex have similar effects on other aqueous emulsions. As reported by Ziegelmeyer⁴, the addition of very small quantities of pectin to natural cow's milk causes separation of the milk into serum and a sediment of an emulsion of albumen which is reversible. Sukurai⁵ observed that the addition of carrageen solutions in very small percentages to milk and also to blood accelerated the rates of separation. It is probable that not only these two natural emulsions of pectin and of carrageen, but also all the products mentioned above behave in a similar manner. The present author found it possible, with the creaming agents described, either to cream or to cause sedimentation (depending on the specific gravity of the emulsified substance) of artificial emulsions and dispersions of organic substances, *e. g.*, emulsions of oils and emulsions of synthetic products of high molecular weights. Furthermore, the addition of very small quantities of these substances causes separation in dispersions of inorganic colloiddally dispersed substances, *e. g.*, dispersions of sulfur with retention of its colloidal state of subdivision. The differences in character of effective creaming agents and of aqueous emulsions which are capable of separating latex into layers point to the likelihood that a very general law is involved.

Of the vast number of substances which are available, only a small number are suitable for concentrating latex in a technical way. Since the various substances differ greatly in chemical constitution, some are hetero compounds, some are homopolar, some are ethers, some are alcohols, some are salts of acids,

etc., the influence of the constituent groups on the properties of the resulting latex concentrates is of fundamental importance. The substances also differ greatly, according to their chemical constitution, in their effect on the stability of the latex concentrates. Great caution must therefore be exercised in choosing the proper creaming agent.

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- ³ By rubber is meant pure rubber hydrocarbon.
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HEVEA LATEX OF LARGE PARTICLE SIZE *

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The purpose of this paper is to report, primarily, the particle size distribution of modified *Hevea* latices. In addition, the purpose is to show that the amount of nitrogen absorbed by the rubber particles in a latex thoroughly washed by aqueous ammonia depends on the surface exposed. Until the careful and complete work of Lucas (*Ind. Eng. Chem.* **30**, 146 (1938)), there were no reliable particle size distribution data on a normal latex by which the distribution curves of modified latices could be compared. Now, as a result of his excellent technique for measuring all of the particles, even the very small ones, we are able to discuss clearly surface and volume changes when these smaller sized particles are removed.

This work was so conducted as to eliminate particle sizes which could not be photographed with microscopical equipment in visible light. It was eventually carried out in such a way as to remove all water-soluble materials not adsorbed on or dissolved in the latex particles which were to be subsequently analyzed for nitrogen.

In the preliminary work the distribution of latex particles creamed with varying amounts of ammonium alginate was studied. Sufficient alginate was used to cause either practically all or only a certain percentage of the rubber in the latex to rise. The actual concentration of alginate employed depends on its quality and the dilution of the latex before creaming; therefore no definite figures which will always work can be given. The amounts used in these experiments are included in the tables and will serve as a guide to what might be employed. In these experiments one creaming cycle was utilized, and hence the small particles originally in the top section of the creaming container still remained there after the operation. However, the additional volume of rubber caused by these smaller particles is so small that it does not materially affect the distribution curve of these fractionated latices.

The creams thus prepared were diluted to 2.5 per cent solids and were then added to an equal amount of 5 per cent purified gelatin solution. After thorough mixing and while the latex-gelatin mixture was still warm, a drop was put on a glass slide, carefully thinned, and fitted with a cover glass. Photomicrographs were taken with a 2-mm. objective and a 3 \times ocular with sufficient bellows extension to give a magnification of 1000 times. The diameter of the particles was then determined by measuring the enlarged photographs with extremely sensitive calipers.

Figure 1 shows contact prints of four of the experiments. The details by which these latices were prepared, together with the results obtained from their measurement, are given in Table I. As the amount of creaming agent is decreased, the average particle volume as well as average particle diameter is increased and the amount of rubber recovered is greatly decreased.

Table II gives the actual measurement as to number of particles, their total volume, and their total diameter for various size intervals. The first column,

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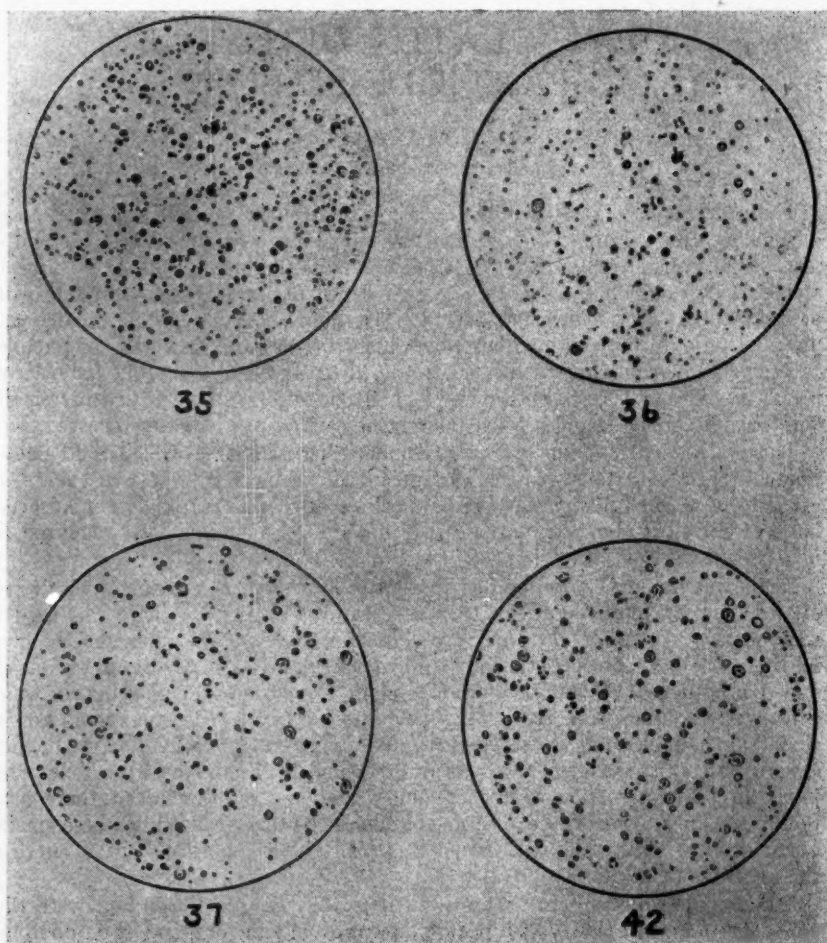
FIG. 1.—Contact prints of four experiments ($\times 1000$).

TABLE I
PARTICLE SIZE DATA OF SUMATRAN HEVEA LATEX

Expt. No.	Creaming agent, part	Av. particle		Approx. % total solids recovered
		Vol., cu. microns	<i>D</i> , microns	
42	0.05	1.44	1.15	10.0
37	0.10	0.64	0.80	60.0
35	0.15	0.30	0.70	85.0
36	0.20	0.30	0.68	90.0

D , represents a size interval 0.05 micron on each side of the value given. Thus the first entry, 2.95 microns, indicates that particles ranging from 3.0 to 2.9 were included in this group.

To give still further information as to distribution of the larger sized particles, several experiments were carried out similar to those described above except that the cream obtained was further washed by rediluting with water and either adding sufficient creaming agent each time to cause the particles above a certain diameter to rise or subjecting the particles to the proper centrifugal force to accomplish the same result.

TABLE II
DISTRIBUTION OF PARTICLES OF SUMATRAN HEVEA CREAMS

D , microns	No. particles				Total vol., cu. μ				$D \times$ no. particles			
	42	37	35	36	42	37	35	36	42	37	35	36
2.95	1	2	0	0	13.2	26.4	0	—	3.0	5.9	—	—
2.85	2	0	0	0	24.4	—	0	—	5.7	—	—	—
2.75	1	1	0	0	10.9	10.9	0	—	2.8	2.8	—	—
2.65	2	2	1	0	19.6	19.6	9.8	—	5.3	5.3	2.6	—
2.55	0	2	0	0	—	17.4	0	—	—	5.1	—	—
2.45	2	1	0	0	15.3	7.6	0	—	4.9	2.5	—	—
2.35	2	0	0	1	13.6	—	0	6.8	4.7	—	—	2.4
2.25	1	1	1	1	5.9	5.9	5.9	5.9	2.3	2.3	2.3	2.3
2.15	7	5	1	3	36.4	26.0	5.2	15.7	15.1	10.7	2.2	6.5
2.05	5	3	1	3	22.6	13.6	4.5	13.5	10.3	6.3	2.0	6.2
1.95	5	4	3	3	19.4	15.4	11.6	11.6	9.8	7.8	5.9	5.9
1.85	13	4	1	1	43.0	13.2	3.3	3.3	24.1	7.4	1.8	1.8
1.75	14	6	6	4	40.0	17.0	17.0	11.3	24.6	10.5	10.5	7.0
1.65	15	18	4	5	35.5	42.5	9.4	11.8	24.9	28.7	6.6	8.2
1.55	9	9	9	3	17.6	17.6	17.6	5.8	13.9	13.9	13.9	4.7
1.45	15	12	14	2	24.5	19.6	22.5	3.2	21.0	17.4	20.3	2.9
1.35	22	16	13	4	28.8	21.0	16.9	5.2	29.8	21.6	17.6	5.4
1.25	14	15	5	5	14.4	15.5	5.1	5.1	18.9	18.8	6.3	6.2
1.15	18	17	5	13	14.4	13.6	4.0	10.4	20.7	19.6	5.8	14.9
1.05	9	30	10	13	5.6	18.6	6.0	7.8	9.5	31.5	10.5	13.6
0.95	13	41	30	24	6.1	19.2	13.4	10.1	12.4	39.0	28.5	22.8
0.85	26	45	63	36	8.7	15.0	20.2	11.5	22.1	38.2	53.5	30.6
0.75	18	57	145	50	4.1	13.1	32.2	11.0	13.5	42.7	108.5	37.5
0.65	18	134	187	89	2.7	20.2	26.8	12.4	11.7	57.0	121.0	57.8
0.55	33	168	247	211	3.0	15.4	21.6	19.0	18.2	93.0	136.0	116.0
0.45	32	35	115	143	1.5	1.7	5.5	7.2	14.4	15.8	51.8	64.6
Total	297	628	861	614	431	406	259	189	344	504	608	417

In the creaming process, the creaming agent, ammonium alginate, was dissolved in water containing 0.5 per cent ammonia and was then added with careful mixing to the normal ammonia latex. This mixture was then diluted to 20 per cent solids and allowed to cream until the cream had reached a value of approximately 50 per cent solids. The serum was removed, and additional water containing ammonia and creaming agent, in the same concentration on the water phase as used before, was added in such a manner as to give 20 per cent total solids. This operation was repeated several times—for example, six times in experiment 21 and five times in experiment W-5. The exact amount of creaming agent to be used depends on the quality of the material. The amounts based on the water for the experiments carried out in this report are given in the tables. However, if the work is repeated, the amount of creaming agent to be used should be such that the recovery of rubber in the cream phase is the important and

guiding principle. In experiments W-5 and 21, 0.01 and 0.04 parts of alginate were needed per 100 parts of water to recover 5 and 55 per cent, respectively, of the rubber in the cream.

The repeatedly centrifuged experiment was carried out in a laboratory centrifuge of low speed. In this case the original latex diluted to 20 per cent solids was centrifuged, and when the machine was stopped, a predetermined percentage of the lower layer was removed. The upper layer was then diluted with 0.5 per cent ammonia water to 20 per cent solids and centrifuged, and the operation was repeated for the same time and at the same rate. Again, the lower layer was removed, an equal amount of distilled water containing 0.5 per cent ammonia was added, and the operation was repeated. This was continued for experiments BE five times. The first serum removed was very cloudy and contained much rubber; the second serum was less cloudy and contained less rubber; the last three serums were practically clear, which indicated that our centrifugal speed was just right to accelerate the rising of all rubber particles now in the system.

In this way three experiments involving a complete removal of water-soluble materials other than those directly absorbed on the rubber were carried out.

TABLE III
REPEATEDLY PURIFIED LATICES

Expt. No.	Description ^a	Av. particle			Rubber recovered (%)	Origin of latex
		Vol. (cu. μ)	D (μ)	Area (sq. μ)		
W-5	Creamed 5 times, 0.01 alginate	1.320	1.27	5.44	5	Malaya
BE-5	Centrifuged 5 times at low speed	1.310	1.31	5.64	18	Malaya
21	Creamed 6 times, 0.04 alginate	0.590	0.95	3.10	55	Malaya
Lucas	Normal	0.035	0.26	0.33	100	

^a In all cases the washing was done with 0.5% NH_3 solution at dilutions sufficient to remove 98% of water-soluble material.

^b It is believed this was Malayan latex.

The per cent rubber recovered was also determined. The details of the preparation and characteristics of these purified large-size particle latices are given in Table III.

Since the size of these particles was relatively large, they were readily photographed. The negatives were then enlarged by projection, and the particles were measured and counted. The results are given in Table IV.

These tables give data on the additive volume of the particles. This additive volume is plotted against particle diameter, and also the data obtained by Lucas (*Ind. Eng. Chem.* 30, 146 (1938)), on a normal ammonia latex (Figure 2 and Table V).

The data in Tables IV and V make it possible to calculate, for the same weight of rubber dispersed in the various latices, the exact area of surface exposed. These results and the nitrogen value of the rubber in the different purified latices are given in Table VI. The amount of nitrogen retained in these washed latices is proportionally very close to the amount of surface exposed.

Hence it is possible to fractionate latex into portions containing different average particle diameters and resulting in definitely different nitrogen values; thus a latex is produced which is well adapted for waterproofing and insulating purposes and will give a highly purified rubber when coagulated.

TABLE IV
PARTICLE MEASUREMENT AND COUNT

<i>N</i>	<i>D</i> (microns)	$\frac{\pi D^3 N}{6}$ (cu. μ)	$\pi D^2 N$ (sq. μ)	Additive vol. (%)	<i>N</i> × <i>D</i>
SIX TIMES CREAMED LATEX (RECOVERY 55%), EXPT. 21					
1	2.18	5.41	14.9	3.4	2.18
1	2.05	4.53	13.1	6.4	2.05
1	1.90	3.50	11.3	8.6	1.90
1	1.83	3.21	10.5	10.6	1.83
2	1.77	5.64	19.6	14.2	3.54
2	1.70	5.14	18.1	17.4	3.40
2	1.63	4.52	16.7	20.3	3.26
3	1.56	6.00	23.2	24.1	4.68
5	1.50	8.85	35.4	29.8	7.50
2	1.43	3.06	12.8	31.7	2.86
6	1.36	8.92	35.0	37.4	8.21
12	1.29	13.40	62.8	46.0	15.50
9	1.23	8.75	42.5	51.6	11.02
13	1.16	10.60	55.0	58.2	15.11
15	1.09	7.40	56.0	63.0	16.40
34	1.02	19.00	111.0	75.1	34.80
17	0.96	7.83	49.0	80.1	16.30
28	0.89	10.35	69.5	86.7	25.00
21	0.82	6.06	44.3	90.6	17.22
24	0.75	5.30	42.3	93.9	18.00
34	0.68	5.60	49.5	97.5	23.20
25	0.61	3.00	29.2	99.4	15.25
7	0.54	0.57	6.5	99.7	3.78
2	0.48	0.11	1.5	99.8	0.96
Total	267	156.75	829.7	—	253.95
Average	—	0.59	3.1	—	0.95
SIX TIMES CENTRIFUGED LATEX (RECOVERY 18%), EXPT. BE-5					
1	2.03	4.40	12.9	2.4	2.03
1	1.95	3.88	11.9	4.5	1.95
2	1.87	6.88	21.9	8.3	3.74
2	1.79	6.00	20.2	11.6	3.58
6	1.72	15.90	55.5	20.3	10.32
5	1.64	11.50	42.3	26.6	8.20
17	1.56	34.00	130.0	45.0	26.50
17	1.48	29.10	117.0	60.9	25.20
9	1.40	12.95	55.5	67.9	12.60
10	1.32	12.10	54.9	74.5	13.20
8	1.25	8.12	39.4	79.0	12.00
24	1.17	20.10	104.0	89.9	28.10
13	1.09	8.91	43.3	94.7	14.30
7	1.01	3.75	32.5	96.7	7.07
6	0.94	2.60	16.6	98.2	5.64
6	0.86	2.00	13.9	99.3	5.16
4	0.78	0.99	7.6	99.8	3.12
Total	138	183.18	779.4	—	182.71
Average	—	1.31	5.64	—	1.31

TABLE IV—Continued
PARTICLE MEASUREMENT AND COUNT

N	D (microns)	$\frac{\pi D^3 N}{6}$ (cu. μ)	$\pi D^2 N$ (sq. μ)	Additive vol. (%)	$N \times D$
FIVE TIMES CREAMED LATEX (RECOVERY 5%), EXPT. W-5					
2	2.19	11.00	30.0	4.9	4.38
2	2.07	9.30	27.0	9.0	4.14
5	1.95	19.45	60.0	17.7	9.75
4	1.84	13.10	42.5	23.5	7.36
11	1.73	30.00	103.0	36.8	19.03
10	1.61	21.50	81.0	47.5	16.10
15	1.49	26.50	104.0	59.2	22.40
18	1.38	24.90	107.0	70.2	24.80
19	1.26	20.00	94.0	79.1	24.00
29	1.15	23.20	122.0	89.4	33.40
22	1.03	12.50	73.5	95.0	22.60
18	0.92	7.35	47.7	98.2	16.60
10	0.81	2.74	20.0	99.5	8.10
3	0.69	0.49	4.2	99.7	2.07
Total	168	222.03	915.9	—	214.73
Average	—	1.32	5.45	—	1.27

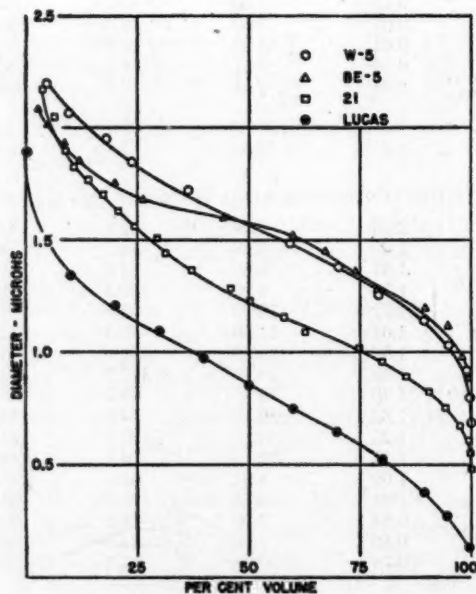


FIG. 2.—Additive volume vs. particle diameter.

TABLE V
PARTICLE MEASUREMENT AND COUNT OF NORMAL LATEX

N	D (microns)	$\frac{\pi D^3 N}{6}$ (cu. μ)	$\pi D^2 N$ (sq. μ)	N	D (microns)	$\frac{\pi D^3 N}{6}$ (cu. μ)	$\pi D^2 N$ (sq. μ)
1	1.85	3.30	10.7	33	0.55	2.86	31.4
4	1.38	5.45	23.9	7	0.51	0.48	5.0
1	1.20	0.91	4.5	24	0.46	1.21	16.3
5	1.15	4.01	20.8	24	0.41	0.85	12.7
1	1.11	0.71	3.8	28	0.37	0.74	12.1
1	1.06	0.62	3.5	74	0.32	1.26	23.8
2	1.02	1.11	6.5	62	0.28	0.71	15.1
11	0.92	4.30	29.2	113	0.23	0.72	18.3
1	0.88	0.35	2.4	199	0.18	0.60	20.8
1	0.83	0.28	2.2	271	0.14	0.38	16.7
1	0.78	0.24	1.9	116	0.09	0.04	2.9
5	0.74	1.06	8.6				
15	0.69	2.67	22.2	Total	1012	36.60	330.4
10	0.64	1.37	12.8	Average	—	0.0358	0.323
2	0.60	0.37	2.3				

TABLE VI

CHARACTERISTICS OF 100 GRAMS OF RUBBER IN FORM OF PURIFIED HEVEA LATEX *

Expt. No.	Area, sq. μ 10^{12}	No. particles 10^{12}	% rubber recovered	N, % on solids
W-5	445	81.9	5	0.038
BE-5	465	82.5	18	0.042
21	566	183.0	55	0.051
18	—	—	99	0.097
Lucas	990	3017.0	100	—

* Volume = 108 cc.

THE SPECIFIC GRAVITY OF RUBBER AND OF SERUM IN HEVEA LATEX *

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INTRODUCTION

Latex may be considered as a disperse system in which two phases can be distinguished, *viz.*, rubber and serum.

Let it be assumed provisionally that a latex particle consists of a homogeneous mass of rubber and disregard any possible difference between the inner and outer layers, and let it also be assumed that the adsorbed layer, about which so little is known, is a part of the rubber particle. When we speak of the specific gravity of rubber, we are really speaking about an imaginary value, *i.e.*, the average of different specific gravities.

Assume that in one part by volume of latex the volume of rubber is a and consequently the serum is $(1-a)$ parts by volume. In this case the weight of latex is obviously:

$$ad_r + (1-a)d_s$$

where d_r is the specific gravity of the rubber and d_s is that of the latex.

Now the rubber in the latex is very finely distributed, so that as long as we are not dealing with processes taking place in very small volumes, we may write:

$$\text{specific gravity of latex} = d_l = ad_r + (1-a)d_s \quad (1)$$

There is thus a relation, expressed by a straight line, between specific gravity and rubber content expressed in units by volume (cc. of rubber per 100 cc. of latex). In Figure 1, this relation is expressed by line QPR. On line BC are found the points representing 100 per cent of rubber.

If the rubber content is expressed in grams of rubber per 100 cc. of latex, a relation, likewise represented by a straight line, is obtained, but in this case it does not extend beyond a certain percentage which equals one hundred times the specific gravity of rubber (Figure 2). The line BC therefore forms a certain angle with the ordinate.

If the rubber content is expressed in grams of rubber per 100 grams of latex, which is the method accepted in practice, the relation between specific gravity and rubber content is no longer expressed by a straight line: in this case a slightly curved line (a hyperbola; cf. Figure 3) is obtained. If a linear equation is desired, it is necessary to substitute, in the ordinate, specific volume for the specific gravity.

However, if we have a grams of rubber per gram of latex and $(1-a)$ grams of serum, the vol. of one gram of latex, *i.e.*, the specific volume, is:

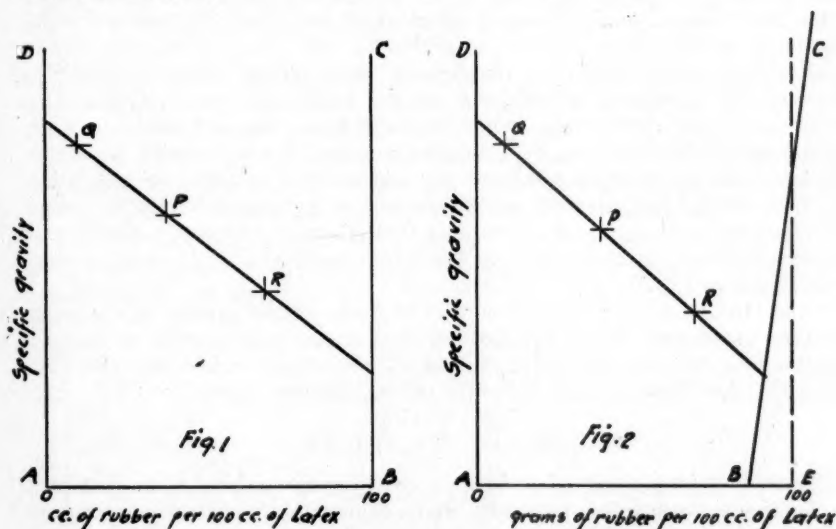
$$v_l = av_r + (1-a)v_s$$

analogous to Equation 1, where v_l , v_r and v_s are the specific volumes of the latex, rubber and serum, respectively.

* Translated by A. H. Krappe for RUBBER CHEMISTRY AND TECHNOLOGY from the *Archief voor de Rubbercultuur*, Vol. 23, No. 2, pages 130-139, 1939.

Since $v_1 = \frac{1}{d_1}$, there cannot be a straight-line relation between d_1 and the dry rubber content (DRC) when the relation between v_1 and DRC, expressed in grams of rubber per 100 grams of latex, is represented by a straight line.

It seemed desirable to investigate these fundamental problems, since errors have appeared repeatedly in the literature and the results obtained have been computed incorrectly.



EARLIER EXPERIMENTS

Numerous investigations of the specific gravity of latex have already been made. Among the oldest of these are those of Vernet¹ and Eaton².

The object of the investigations was to study the relation between DRC and specific gravity in order to be able, by a simple measurement of the specific gravity of an unknown latex, to determine the DRC value and thus to render unnecessary the more complicated coagulation method.

This work is, however, concerned only with the specific gravities of the pure components, rubber and serum.

The practical applications mentioned above are disregarded for the present.

Since a direct determination of the required specific gravity is not possible, we shall have recourse to an indirect method.

Scholz and Klotz³ have carried out specific gravity determinations (pycnometrically) and DRC determinations with a large number (91) of samples of latex. The observations were plotted graphically, and the points found were, as far as possible, connected by a line. The point of intersection with the ordinate indicated the mean specific gravity of the serum (1.023), and the point of intersection with the line for 100 per cent of rubber represented the mean specific gravity of rubber (0.901).

Apart from the fact that this involved an error, namely, that of presupposing a linear relation between specific gravity and DRC expressed as percentages

by weight, there is still another objection to this method, namely, that different kinds of observations are combined. It is, however, certain that the specific gravity of rubber and that of serum differ from sample to sample. Observations with latex A must therefore not be combined with observations with latex B. A large number of observations does not eliminate the error.

Rhodes⁴ proceeded in the same manner, except that he experimented with 852 samples, that he divided his observations into eleven groups according to the DRC found, and then averaged each group. In this way he obtained eleven points in his DRC-specific gravity diagram, all of which lay more or less on a straight line.

After having first committed the error of using weight values of DRC, he corrected this mistake in a subsequent article⁵ and found by extrapolation the mean specific gravity of rubber to be 0.9064 and that of serum 1.0200.

De Vries⁶ proceeded again in a different manner. He determined, for a certain latex, the specific gravity of the acetic acid serum obtained after coagulation, and from this he computed the specific gravity of the original serum as it must have been in the latex, on the assumption that in coagulation one is dealing with simple separation. By this method he found the specific gravity of serum to range from 1.0226 to 1.0170.

If the DRC of a given latex is known and if the specific gravity of the serum has been determined in the manner described above, it is possible to compute the specific gravity of the rubber. De Vries thus found values between 0.913 and 0.922. The value 0.914 is, according to him, the most frequent.

ORIGINAL EXPERIMENTS

The method adopted by us depends on centrifuging the latex to be examined. In this way a cream with a high DRC and a skim with a low DRC are obtained.

By determining the DRC and at the same time the specific gravity of both cream and skim, one obtains, on the graph of Figure 2, two points, Q and R. A straight line through Q and R cuts the line BC at a certain point, from the position of which the specific gravity of the rubber phase may be read off. Here the original latex is represented by point P.

As will be easily seen, P, Q and R lie on a straight line, because centrifuging is a purely mechanical process which changes only the proportion of the two components, serum and rubber. On the other hand, the fact (repeatedly found experimentally) that the three points lie, within experiment errors, approximately on a straight line, indicates clearly that, for this case, we may indeed consider latex as a two-component system (cf. p. 422). The presence of small resin globules or other possible particles with specific gravity different from that of rubber does not therefore have a disturbing influence.

Bearing in mind this source of error, we have always allowed the ammoniated latex to stand for some time. Magnesium ammonium phosphate, frequently present in considerable quantities, has then an opportunity to precipitate. In yellow latices, *e.g.*, latex derived from Tjirandji I clones, a pronounced yellow layer formed at the bottom of the bottle. Only the pure white upper layer was used for the examination. Furthermore, we never examined latex derived from trees not previously tapped or from trees tapped in an abnormal manner.

After some experimenting it was decided that the following method was the most suitable.

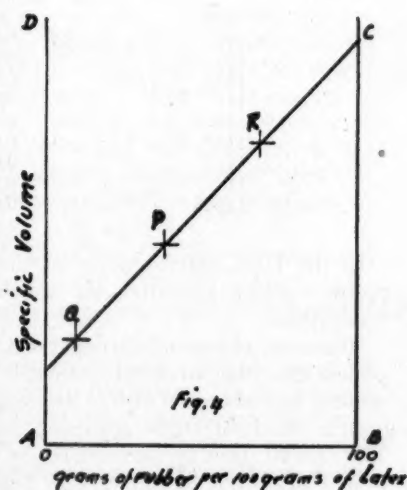
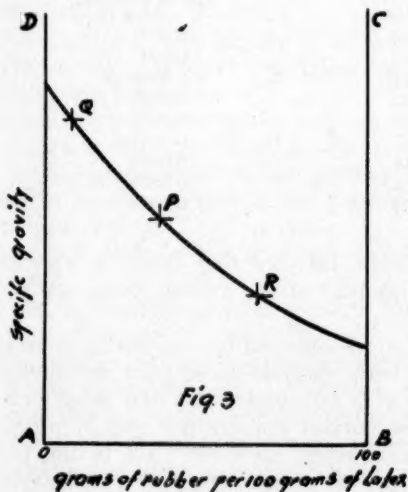
The ammoniated latex to be examined was first filtered, and 800 cc. were diluted with water to the point where the DRC was approximately five per cent.

Fifty cc. of concentrated ammonium hydroxide were added to the water used for dilution, a quantity which seemed sufficient to keep the latex in good condition for a few days. Centrifuging was carried out in a small milk centrifuge constructed of the De Laval type. The flow velocity of the latex was regulated so that a thick cream flowed in drops or in a small jet from the cream pipe of the centrifuge. After the entire quantity had flowed through once, the skim was centrifuged twice more. A skim with a DRC of 1-1.3 per cent and a cream of 50-53 per cent was finally obtained.

Both cream and skim were kept until the following day to allow air bubbles formed by centrifuging to rise. After filtering through a raw cotton stopper, the DRC and specific gravity were determined. At the same time the original latex and, in some cases, also a sample of the diluted but not centrifuged latex were also determined.

The specific gravity determination was carried out at 30.0°C. (thermostat) by means of bottle-shaped pycnometers. Double determinations were not allowed to differ by more than one unit of the fourth decimal.

The determination of DRC was carried out in the manner commonly adopted at the test laboratory. The duplicate results differed in general by only some hundredths of one per cent.



CALCULATIONS

For calculating the specific gravity of the rubber phase use was made of the relation between specific volume and DRC (percentage by weight) as expressed in Figure 4.

The method of illustration adopted in Figure 2 has probably some advantages over a graph; for calculation, Figure 4 is preferable.

The specific volume of the rubber phase is then computed as follows:

$$\text{sp. vol. rubber} = \text{sp. vol. skim} + \left\{ (100 - \text{DRC skim}) \frac{\text{sp.vol. cream} - \text{sp.vol. skim}}{\text{DRC cream} - \text{DRC skim}} \right\}$$

PRECISION ATTAINED

As was pointed out, the precision in the determination of specific gravity is 0.0001.

From the ratio: DRC/sp.gr., it appears that the difference of 0.0001 in the specific gravity agrees with a difference of 0.1 per cent in the DRC. The DRC determinations must therefore be precise to at least 0.1 per cent.

This precision was certainly attained in our determinations. We realize, however, that the DRC does not represent the content of pure rubber hydrocarbons present in the latex⁷. The difference between the two represents in the main the proteins precipitated during coagulation.

As for the proteins in latex, two parts may be distinguished: one is adsorbed by the rubber, the other is in the serum. The former is entrained with the rubber during centrifuging and therefore constitutes a part of the rubber phase; it necessarily has an influence on the determination of specific gravity. The latter is practically entirely removed by the method adopted by us, *viz.*, strong dilution of the latex and concentration until a DRC of more than 50 per cent is reached.

TABLE I

No. latex	Specific gravity by method I	Specific gravity by method II
108	0.9039	0.9041
109	0.9044	0.9045
110	0.9042	0.9044
111	0.9033	0.9035
112	0.9040	0.9043
114	0.9047	0.9048
115	0.9046	0.9048
117	0.9052	0.9055
118	0.9043	0.9045

In the DRC determination of the cream, only the first part, *i.e.*, only the proteins, which constitute the mechanical part of the rubber phase, are thus precipitated.

Numerous nitrogen determinations of crepes obtained by coagulation of cream proved that this adsorbed protein is a fairly constant factor; for the nitrogen content was always 0.14-0.15 per cent. If it is assumed that the usual factor, 6.25, is valid for rubber proteins, crepe contains about 1 per cent of protein. The specific gravity determined by us therefore does not refer to the pure rubber phase but to rubber with 1 per cent of protein, *i.e.*, rubber as it occurs in latex with its adsorption skin.

It might be objected that this reasoning is valid only for cream, but not for skim, of which however the DRC and specific gravity were also determined.

It is true that the nitrogen content of the skim is large, amounting to 0.8-0.9 per cent, based on the rubber; however, based on the latex it is too small to cause a serious error in calculating the specific gravity of rubber.

It is evident then that there are great advantages in strongly diluting latex before centrifuging. In addition to removing unadsorbed proteins, it has the additional advantage that the difference in the DRC of cream and skim is very large, as a result of which extrapolation for the specific gravity of the rubber phase becomes more exact.

Taking into account all possible sources of errors, we reach the conclusion that the possible error in the final result is ± 0.0002 .

Table I shows that we might also have started from the DRC and specific gravity of diluted but not centrifuged latex.

The specific gravities in column II have been computed from the data for cream and skim (points R and Q in Figures 1-4); the specific gravities in column III have been computed from the data for cream and diluted latex (points R and P in Figures 1-4).

It will be seen that the figures in column III average 0.0002 higher than those in column II. It cannot be denied that here a small consistent error was made; it remains, however, within the limits of precision set up above.

By means of Table I we may also verify what has been said on p. 423, *viz.*, that points P, Q and R lie approximately on a straight line.

When the specific gravity of the rubber of a given latex sample is known, it is very simple to compute the specific gravity of the pure serum by means of the DRC and the specific gravity of the latex.

DISCUSSION OF THE RESULTS

The specific gravities of rubber and serum found experimentally are given in Table II.

The average specific gravity of rubber is 0.9042 and that of serum is 1.0237.

The variations in specific gravities are small for rubber but larger for serum. With respect to the latter, it must be borne in mind that it is not impossible that the latex has been mixed with rain water. Although we have always taken care that in our experiment garden Tjiomas latex was collected only on dry days, an extremely low specific gravity such as that found for the serum of latex No. 97 suggests that in that case dilution of latex with water is not wholly out of question.

Furthermore latex was obtained exclusively from trees tapped regularly and normally.

From the specific gravities given in Table II, it is impossible to deduce the slightest regularity or correlation.

The specific gravity of rubber is not characteristic of the clone, nor have we been able to find any influence of the age or origin of the tree. It is, however, possible that a more detailed examination will bring to light some such regularity.

This may also be said of the specific gravities of serum. Further examination is in this case easier to carry out. By neglecting the small variations in the specific gravities of rubber, it is possible to compute an approximate specific gravity of serum with only one DRC and one specific gravity determination of the latex. There can be no doubt that in that case the tapping method, rainfall, season, etc., will influence appreciably the specific gravity of the serum.

For the present we wish to say a few words concerning the possibility of computing the DRC of a given latex by means of a specific gravity determination.

If we are satisfied with moderate precision (1-2 units of the DRC in per cent) and if the latex is not diluted with water, it seems to us quite possible to compile a specific gravity-DRC table; but whether a general table is possible for all seasons and for all plantations must be determined by a detailed examination.

In the preceding discussion we have assumed the possibility of determining the specific gravity of latex with a precision of three decimal places. Whether

TABLE II

No.	Grade of latex	Clone	Latex		Specific gravity of serum (calculated)	Cream		Skim		Specific gravity of rubber (calculated)
			DRC	Total solids		DRC	Specific gravity	DRC	Specific gravity	
90	Tjomas	—	35.25	—	1.2200	51.18	0.9482	1.02	0.9983	0.9041
91	"	—	31.14	35.86	1.0354	47.74	0.95173	1.64	0.99805	0.9042
92	"	—	36.76	39.33	1.0289	52.14	0.9480	1.46	0.9986	0.9037
94	"	Tjir 1	31.34	33.95	0.98278	48.99	0.95197	1.36	1.00070	0.9043
95	"	Tjir 16	28.61	31.26	0.98699	49.24	0.95161	1.30	1.00049	0.9048
96	"	BD 5	39.21	42.02	1.0253	49.22	0.95138	1.53	1.0000	0.9042
97	"	BD 10	29.67	31.46	0.97800	52.28	0.94768	1.02	0.99974	0.9039
98	"	BR 2	32.57	35.48	0.98028	49.83	0.95062	1.24	1.00005	0.9045
99	"	BD 17	41.22	44.10	0.97154	53.39	0.94690	1.42	0.99953	0.9042
100	"	War. 1	34.16	36.96	0.97814	48.71	0.95173	1.29	1.00007	0.9045
101	"	—	42.37	44.83	0.96945	50.91	0.94958	1.77	0.99934	0.9046
102	Pasir Oetjing 1904	—	38.90	41.46	1.0212	52.09	0.94788	1.12	1.00026	0.9034
103	Diasinga 1906/1907	—	40.66	—	1.0236	56.55	0.94385	1.56	0.99995	0.9038
105	Tjiseroe	—	38.72	41.26	—	55.05	0.94544	1.31	0.99980	0.9043
107	Moesi en Landas	Avros 163	35.87	38.39	0.97696	55.97	0.94431	1.09	1.00021	0.9038
108	"	BD 10	39.12	41.62	1.0233	56.48	0.94386	1.08	1.00024	0.9039
109	"	Avros 49	37.11	39.44	1.0255	55.63	0.94493	1.09	1.00010	0.9044
110	"	BD 5	38.98	41.67	0.97431	53.96	0.94659	1.11	1.00043	0.9042
111	"	Tjir 1	44.47	47.01	1.0257	55.80	0.94414	1.32	0.99985	0.9033
112	"	Tjir 16	41.07	43.60	0.97162	53.08	0.94733	1.11	1.00041	0.9040
114	Tjomas	BJ II I BI III	35.63	38.00	0.97866	54.17	0.94659	1.18	1.00010	0.9047
115	"	Tt 28 BI I	29.94	32.27	0.98392	52.35	0.94835	0.98	1.00052	0.9046
116	"	Tt 29 BI I	26.83	29.88	0.98909	53.41	0.94784	0.83	1.00102	0.9052
118	"	BI III	32.89	35.24	0.98085	54.47	0.94612	0.98	1.00053	0.9043

Average = 1.0237

Average = 0.9042

 $\sigma = 4.38 \times 10^{-4}$

Although it is not justifiable to calculate DRC and total solids to two decimal places, this has been done here because, in the calculations, these values were not averaged.

σ is a measure of the deviations of individual observations.

$$\sigma = \sqrt{\frac{\sum d^2}{(n-1)}}$$

this can be accomplished with the latexometers or hydrometers obtainable in the market, we do not venture to say.

The last word in the matter must be left to the technologist.

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CONTRIBUTIONS TO THE ANALYSIS OF RUBBER

IV. DETERMINATION OF MANGANESE IN CRUDE RUBBER; IN RUBBER MIXTURES AND IN FILLERS *

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I. INTRODUCTION

It has been proved by numerous investigations that manganese compounds destroy rubber. Thus Bruni and Pellizola¹ showed that stickiness which crude rubber may exhibit is attributable to the presence of manganese. Whereas grades of plantation rubber in normal condition contain 0.0001 to 0.0003 per cent of manganese, grades with a strong tendency to become uniformly sticky were found to contain 0.01 to 0.02 per cent of manganese. In grades which became slightly and irregularly sticky, the manganese contents were found to be 0.001 to 0.005 per cent.

In contrast to this, Kirchhof² found consistently lower manganese contents in samples of rubber of different degrees of stickiness than the limiting values assigned by Bruni and Pellizola. However, Kirchhof found that the iron contents of these samples of sticky rubber were five to ten times as great as the iron content of sound grades, and he suggested that these high percentages of iron played an active part in the appearance of stickiness, for it seemed possible that the iron was present originally in the ferrous state.

Furthermore Kirchhof confirmed the damage done to vulcanized rubber by manganese. His observations led him to the conclusion that manganese contents of the order of magnitude of 0.05 per cent (based on the rubber content of the particular mixture) are to be regarded as dangerous even in vulcanized rubber, particularly when relatively large percentages of iron oxide also are present.

Taylor and Jones³ carried out aging tests with various metallic salts. These investigators found that when 0.1 per cent of manganese oleate was present, the deleterious effects of manganese were quite evident in aging tests by the Bierer-Davis method but not by the Geer-Evans method.

Extensive aging tests were carried out by Sackett⁴ with rubber mixtures prepared from crude rubber containing 0.0218 per cent of manganese. This high manganese content resulted from the use on the plantation of water containing manganese. By mixing this rubber with normal crude rubber, rubber mixtures with lower manganese contents were prepared.

Rubber mixtures containing 0.0044 per cent of manganese but no fillers, and vulcanized with mercaptobenzothiazole or diphenylguanidine, showed considerable losses in tensile strength when aged by the Bierer-Davis and Geer-Evans methods. The losses in tensile strength of a mixture containing no accelerator were much less. Furthermore, with a tire tread mixture vulcanized with mercaptobenzothiazole as accelerator and containing 0.01 per cent of manganese, almost no losses in tensile strength occurred under the same conditions.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 15, No. 11, pages 179-182, November 1939.

Although the foregoing facts show clearly the harmful effects of manganese, the problem as to the maximum allowable manganese content still remains unsettled. The only impression obtained is that manganese has a more deleterious effect in crude rubber than it does in vulcanized rubber mixtures.

Since, as with copper, not every manganese compound is harmful, the fixing of a maximum allowable percentage of manganese is always a speculative one. In the Netherlands Government Rubber Institute, the manganese content of a material signifies only manganese which is soluble in concentrated nitric acid (density 1.4), since manganese compounds which are not soluble in this acid are so stable that they have no poisonous effect on rubber.

II. METHODS OF DETERMINING MANGANESE CONTENTS

1. METHODS OF THE NETHERLANDS GOVERNMENT RUBBER INSTITUTE

For many years the two methods described below have been used by the Netherlands Government Rubber Institute.

(a) *Determination of Manganese in Fillers.*

Five grams of sample are treated with 25 cc. of nitric acid (density 1.4) in a beaker (Griffin type), the mixture is evaporated almost to dryness on a steam bath, the residue is taken up in 40 cc. of water, 3 cc. of 20 per cent sulfuric acid are added, the mixture is filtered through an asbestos Gooch crucible, 1.5 cc. of 10 per cent silver nitrate solution is added to the filtrate and the solution is boiled with a few strips of filter paper. If the content of chlorine compounds is high, the chlorine content is determined beforehand, and the extra quantity of silver nitrate necessary to precipitate this chlorine is added. The solution is filtered once more, is diluted with water to 100 cc., 20 cc. of this solution (corresponding to 1 gram of original sample) are placed in a white porcelain crucible, 5 cc. of nitric acid (density 1.2) and approximately 0.5 gram of potassium persulfate are added, the crucible is covered with a watch glass and is heated on a steam bath for 10 minutes.

Approximately 25 cc. of water are placed in a second crucible and enough 0.01 N potassium permanganate solution is added from a micro-burette or from a calibrated pipette (1 cc. capacity) to make the color the same as that of the sample.

Each 1 cc. of 0.01 N potassium permanganate consumed represents 0.011 per cent of manganese in 1 gram of sample.

If more than 1 cc. of permanganate solution is necessary, the solution of the sample is diluted with water and the manganese is determined in an approximate way. The determination is then repeated with a smaller quantity of the filtrate. This smaller volume is diluted with water to 20 cc., care being taken that 0.5 cc. of 20 per cent sulfuric acid and 0.3 cc. of 10 per cent silver nitrate solution for each 20 cc. of solution are present.

(b) *Determination of Manganese in Crude Rubber, in Rubber Mixtures, in Compounding Materials and in Rubberized Fabrics.*

Five grams of sample are incinerated in a porcelain crucible. If the ash content is greater than 5 per cent, the ash is treated as in the foregoing procedure for fillers. If the ash content is less than 5 per cent, the ash is treated with a few cc. of nitric acid (density 1.4), the mixture is evaporated on a steam bath,

the residue is taken up in a mixture of 4 cc. of nitric acid (density 1.2), 10 cc. of water, 0.5 cc. of 20 per cent sulfuric acid and 0.3 cc. of 10 per cent silver nitrate solution, the mixture is heated on a steam bath for several minutes, is filtered, the filtrate is diluted with water to 25 cc., approximately 0.5 gram of potassium persulfate is added, and the determination is carried out in a porcelain crucible, as before.

If the color of this solution is similar to that of the control solution containing 1 cc. of 0.01 *N* potassium permanganate, the sample contains 0.0022 per cent of manganese. It should be mentioned that the method just described was developed mainly from a paper by Wester⁵. According to Wester, the ash is taken up in 25 per cent hydrochloric acid and, after addition of some sulfuric acid, is concentrated and the excess of sulfuric acid is evaporated. The manganese is then determined in closed colorimetric tubes, since the colors obtained with quantities of 0.02 to 0.03 mg. of manganese become paler on exposure to air.

It was found that, in the case of crude rubber, concentration with nitric acid gives the same results and therefore that the manganese is completely dissolved by nitric acid.

It was further proved that as small a quantity as 0.01 mg. of manganese can be determined precisely by the method of the Rubber Institute if the comparison with 0.01 *N* potassium permanganate is made immediately after oxidation by potassium persulfate.

2. NITRIC ACID-LEAD PEROXIDE METHOD

The nitric acid-lead peroxide method for the determination of manganese has been used by several investigators.

Kluckow and Siebner⁶ employed the following method. The ash from 1000 sq. cm. of fabric, 10 grams of organic dye or 1-2 grams of inorganic pigment or filler is treated with 35 cc. of nitric acid (density 1.2), enough lead peroxide to cover a knife point and a little silver nitrate solution; the mixture is boiled for 5 minutes, then is transferred to a measuring cylinder, is allowed to stand in darkness to settle, and the clear solution is poured into a Duboscq plunge cylinder. Another plunge cylinder is filled with a manganese solution of known concentration. It is advantageous to separate the lead peroxide-silver nitrate precipitate by centrifuging, for in this way a clear solution is obtained for the required comparison.

Comparative tests of the method of Kluckow and Siebner and that of the Rubber Institute were carried out, except that the colorimetric measurements were made in the porcelain crucible. Furthermore the method of the Rubber Institute was carried out with lead peroxide as oxidizing agent in the following way.

Twenty cc. of filtrate, 10 cc. of nitric acid (density 1.2) and enough lead peroxide to cover the point of a knife were boiled for 5 minutes, the mixture was transferred to a measuring cylinder, was kept in darkness for 1 hour, and the manganese was determined in the porcelain crucible. The results are summarized in Table I.

It is evident from Table I that concordant results are obtained with potassium persulfate and lead peroxide. However, when lead peroxide was used in the Rubber Institute method, turbid solutions were frequently obtained, even after prolonged standing and cautious decantation from the deposit. Table I shows also that this trouble is still greater in the method of Kluckow and Siebner, and that in this case centrifuging is necessary.

Since the color of the solution which has been oxidized by potassium persulfate is better suited for the determination in a porcelain crucible, this method is recommended. It should be added that Kehren⁷ too recommends oxidation by potassium persulfate for determining manganese in textiles.

TABLE I

DETERMINATION OF MANGANESE BY THE KLUCKOW-SIEBNER METHOD AND BY THE NETHERLANDS GOVERNMENT RUBBER INSTITUTE METHOD

	Kluckow-Siebner method		Netherlands Institute method	
	A	B	With potassium persulfate	With lead peroxide
Zinc oxide:				
No. 20	Turbid	0.002	0.002	0.002
No. 22	Turbid	0.011	0.012	0.012
No. 23	Absent	Absent	Absent	Absent
Whiting:				
No. 4	0.015	0.016	0.015	0.015
No. 7	0.019	0.021	0.019	0.020
Barium sulfate	Turbid	0.004	0.004	0.004
Iron oxide:				
No. 2	0.007	0.008	0.008	0.008
85 per cent.....	Turbid	0.004	0.004	0.004
96 per cent.....	Turbid	± 0.001 *	0.0015	0.0015
98 per cent.....	Turbid	± 0.003 *	0.0025	0.0025

A = after having stood for one hour.

B = after having stood for one hour and then centrifuged.

* The color was not exactly the same as that of the permanganate. The results in Table I are expressed in percentage.

3. ESTIMATION OF THE TOTAL MANGANESE BY DECOMPOSITION

Several investigators have decomposed the ash by a soda-potash mixture. Some comparative results by this method are shown in Table II.

TABLE II

DETERMINATION OF MANGANESE CONTENTS

Material	After evaporation with nitric acid (Rubber Institute method) (Per cent)	After decomposition by soda-potash mixture (Per cent)
Camera cloth No. 1.....	0.0011	0.0024
Camera cloth No. 2.....	0.0004	0.0015
Mantling	0.0022	0.0043
Bentonite clay	0.0063	0.010
Devolite clay	0.0003	0.012
China clay	0.0004	0.011

It is evident from the data in Table II that, after decomposition by a soda-potash mixture, the manganese contents are considerably higher, especially with clays. However, it seems certain that manganese compounds which are occluded in silicates can have no harmful effect. It would be very desirable if a reliable method for the decomposition of manganese were developed, as has already been mentioned in connection with the determination of copper⁸.

4. OXIDATION BY POTASSIUM PERIODATE

Potassium periodate was used by Richards⁹ for the oxidation of colorless manganese ions to red permanganate ions. This oxidizing agent has been utilized by other investigators as well. However, different acids and different times and temperatures were used in the oxidation process.

Bishop and Sekar¹⁰ dissolved the ash from crude rubber in a mixture of nitric acid and sulfuric acid. After dilution with water, the product was filtered and potassium periodate was added to the filtrate; after the mixture had stood overnight, the manganese was determined colorimetrically.

Harry¹¹ treated the ash with nitric acid, concentrated the mixture, added hydrochloric acid and sulfuric acid, evaporated until all sulfuric acid vapors were expelled, the residue was taken up in water, was filtered, the filtrate was concentrated to 10 cc., 0.3 g. of potassium periodate was added and the mixture was boiled for 30 minutes.

According to the standard method of the American Society for Testing Materials¹², the ash is taken up in a mixture of 15 cc. of 85 per cent phosphoric acid and 5 cc. of concentrated nitric acid, the mixture is diluted with water, is filtered,

TABLE III
DETERMINATION OF MANGANESE

Sample	1 Potassium periodate (Per cent)	2 Potassium persulfate with phosphoric acid (Per cent)	3 Rubber Institute method with potassium persulfate (Per cent)
Mending fabric No. 1.....	0.0005	0.0011	0.0011
Mending fabric No. 2.....	Absent	0.0004	0.0004
Mantling	0.0020	0.0022	0.0023
Bentonite clay	0.0065	0.0065	0.0066
Devolite clay	Absent	0.0004	0.00004
China clay	Absent	0.0004	0.0004
Iron oxide	± 0.005 *	0.065	0.070

* Brown precipitate.

the filtrate is made up to 100 cc., 0.5 gram of potassium periodate is added, the mixture is boiled for 1 minute, and kept warm for 5 to 10 minutes.

In the Netherlands Government Rubber Institute, the determination was carried out precisely in the way described above for mineral fillers, except that potassium periodate was used instead of potassium persulfate. Since after 15 minutes' heating on a steam bath the solutions were almost colorless, heating was continued for 2 hours and the manganese was then determined. Table 3 shows some typical results which were obtained.

It was further stated by Kehren¹³ that the addition of orthophosphoric acid favors the formation of permanganate, since manganese dioxide dissolves in phosphoric acid, with formation of violet colored tervalent manganese salts. In view of this, another series of determinations was carried out with potassium sulfate to which two drops of 75 per cent orthophosphoric acid were added. The results are summarized in Table III.

From the data in Table III it is evident that when potassium periodate is used, small quantities of manganese escape detection. If iron is present in the solution, a brown precipitate is formed.

The values which were obtained when phosphoric acid was added agree with those obtained when it was not added. In the determination of manganese in

iron oxide, it was noticed that the color of the sample with phosphoric acid was better; moreover the color seemed to be somewhat more stable, in fact it had become hardly any paler after standing in the open crucible for two hours. The addition of orthophosphoric acid is therefore recommended.

III. RESULTS OF THE MANGANESE DETERMINATIONS

Formerly the amount of manganese allowed was set by the Netherlands Government Rubber Institute at 0.01 per cent, but more recent experience has shown that the manganese contents of fillers, compounding ingredients, etc., are generally considerably lower than this tolerance. Only fillers such as whiting, red iron oxide, clay and rubber mixtures containing these materials are found frequently to contain more than 0.01 per cent of manganese.

TABLE IV

MANGANESE CONTENTS OF VARIOUS RAW MATERIALS AND PRODUCTS IN THE RUBBER INDUSTRY

Material	Number of samples analyzed	Percentage of manganese					
		Absent	None to 0.001	0.001 to 0.002	0.002 to 0.005	0.005 to 0.01	Higher than 0.01
Crude rubber (first latex) ..	60	4	56	0	0	0	0
Sulfur	3	1	2	0	0	0	0
Accelerator	46	30	12	2	0	2 ^a	0
Antiaiging agent	22	16	6	0	0	0	0
Plasticizing agent	21	16	3	1	0	0	1 ^b
Organic blue color	6	2	2	1	1	0	0
Organic red color	10	7	3	0	0	0	0
Organic green color	5	0	2	0	2	1	0
Barytes	43	0	32	6	3	2	0
Devolite clay	16	13	3	0	0	0	0
Bentonite clay	6	0	0	2	2	2	0
Talc	10	1	7	2	0	0	0
Whiting	11	0	2	1	1	1	6 ^c
Zinc oxide	10	7	1	0	1	0	1 ^d
Titanium dioxide	3	3	0	0	0	0	0
Gas black	24	21	1	1	1	0	0
Red iron oxide	13	0	1	0	4	2	6 ^e
Silicic acid	10	1	4	4	1	0	0
Rubberized fabric	35	0	31	4	0	0	0
Plastic packing ring	52	2	35	15	0	0	0
Rubber flooring	54	6	12	4	8	20	4 ^f

a = 0.007, 0.0066. b = 0.022. c = 0.012, 0.013, 0.025, 0.027, 0.033, 0.037. d = 0.013.
e = 0.013, 0.014, 0.014, 0.025, 0.031, 0.034. f = 0.012, 0.013, 0.013, 0.016.

In Table IV, the results of determinations of the manganese contents of a number of fillers and compounding ingredients and other products of the rubber industry are summarized. The analytical results are divided into six groups, according to the manganese contents.

It is evident from the data recorded in Table IV that the manganese contents of various materials differ considerably, but that in general they are very low, in fact manganese contents greater than 0.002 per cent were found in only a few cases. Crude rubber, i. e., first latex crepe, first latex sheet and evaporated latex, contained only 0.0001 to 0.0002 per cent.

The manganese contents of the various compounding ingredients were considerably below 0.002 per cent, and in most cases manganese could not be detected. On the contrary, the organic coloring agents and mineral fillers contained

in many cases 0.002 to 0.005 per cent of manganese, and even this range was considerably exceeded by some of the samples of whiting, colloidal clay and iron oxide. The samples of rubber flooring showed particularly high manganese contents, and in many cases values above 0.005 per cent were found. These high values are attributable to the use of impure fillers, such as whiting. For the sake of satisfactory natural aging of rubber flooring, it would certainly be desirable that an allowable limit be placed on its manganese content.

On the basis of the experience gained from the analyses summarized in Table IV, the Netherlands Government Rubber Institute has recently established the following percentages of manganese as the maximum allowable limits.

Product	Maximum allowable percentage
Crude rubber (first latex).....	0.001
Accelerators, antiaging agents (antioxidants), plasticizing agents, sulfur, carbon black, and rubberized fabrics.....	0.002
Organic coloring agents, mineral fillers, rubber mixtures and rubber articles.....	0.005
Whiting, red iron oxide.....	0.01

IV. SUMMARY

A scheme for the determination of manganese in mineral fillers, compounding ingredients, crude rubber, rubber mixtures and rubberized materials is described.

It is shown that with this method the use of potassium persulfate and two drops of orthophosphoric acid, as proposed by Kehren for the oxidation of colorless manganese ions to red permanganate ions, is advisable. When potassium periodate is used, small quantities of manganese escape detection.

It is further shown that there is no appreciable difference between concentration with nitric acid and evaporation with hydrochloric acid and a little sulfuric acid. If, however, the ash is decomposed by soda-potash mixture, the manganese contents are considerably higher. Doubtless these higher values can be accounted for by manganese compounds which are occluded in silicates, and which can be regarded as harmless. A reliable method for the decomposition of the manganese compounds is therefore desirable.

The results of analyses of the manganese contents of a large number of various materials are tabulated, and the maximum manganese contents of various materials allowed by the Netherlands Government Rubber Institute are given.

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EXPERIMENTS ON THE DETERMINATION OF THE ACTIVITY OF CARBON BLACK BY ITS POWER OF ADSORBING CARBON TETRACHLORIDE VAPOR *

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On the basis that a material like carbon black must, because of its very high ratio of surface area to volume, possess very high adsorptive capacity, several investigators have attempted to establish the relationship between the adsorptive capacity of carbon black and its activity in rubber.

Spear and Moore¹ used aqueous solutions of malachite green, Victoria blue and hexamethylenetetramine; Beaver and Keller² used iodine in aqueous potassium iodide; Goodwin and Park³ used iodine in carbon tetrachloride and also an aqueous solution of methylene blue; Carson and Sebrell⁴ used iodine, benzoic acid, mercaptobenzothiazole and diphenylguanidine. All these workers tested various types of carbon black.

If one examines critically the data of these several investigators from the point of view of the relation between the adsorptive capacity of a carbon black and its activity in rubber, it will be evident that the investigations do not lead to any reliable method whereby the behavior of carbon black in rubber can be judged by its adsorptive capacity.

In view of this, an investigation was undertaken with the aim of developing a method of estimating the activity of a carbon black in rubber by its adsorptive capacity for the vapors of volatile organic liquids. In preliminary experiments, attempts were made to determine the heats of wetting and the electrical conductivities of carbon blacks. These experiments did not, however, give any promising results. Accordingly in the next experiments, the adsorptive capacities of both so-called active and inactive carbon blacks for the vapors of highly volatile liquids such as benzene, carbon disulfide and carbon tetrachloride were studied.

The method for determining adsorption properties of carbon black was to pass air saturated by the vapors of the organic liquid through a layer of black until the sample reached a constant weight.

Figure 1 shows the scheme of the apparatus. The water pump (16) draws in air from the atmosphere; the quantity of which is measured by the water meter (1), a full turn of the large hand indicating the flow of one liter. Behind the water clock is a calibrated flow-meter. The air, after being thoroughly dried in the tower by calcium chloride (3) enters the scrubbers (8), which are placed in series. In these scrubbers the air is saturated with the vapor of the given liquid. The scrubbers are placed in series in order to obtain complete saturation at the particular temperature. In these scrubbers, thorough contact of air with liquid is obtained through division into diminutive bubbles, by means of a plate of a porous glass through which the air must force itself.

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These scrubbers are placed in the thermostat (7) maintained at 15°C . Because the room temperature is usually higher, water of about 120°C . is sent from a faucet through the thermostat. To bring the water in the thermostat to 15°C ., the thermostat is heated with a micro-burner (6), connected with thermoregulators (9). This maintains the temperature of the water in the thermostat at $15^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$.

The air saturated with the vapors of the liquid passes through a Woulff bottle (12) filled with glass wool to catch any entrained fog, then through tube U (13).

One arm of the tube is filled with carbon black, the other arm with glass wool, which prevents the carrying away of the carbon black dust.

Tube U is maintained at $20^{\circ}\text{C} \pm 0.5^{\circ}$. After leaving this tube, the air passes to a manostat (14), which equalizes small variations in the suction. By means of a safety valve (15) it is possible to regulate the rate of flow of air by setting at a proper level, an air-tube, immersed in cold sulfuric acid solution. This

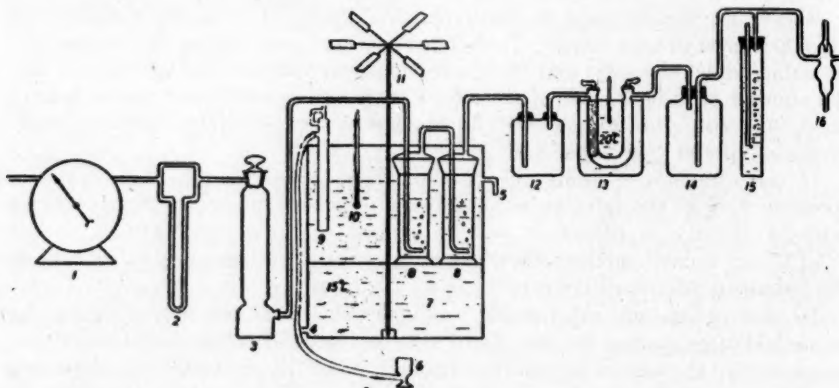


FIG. 1.

valve also functions as a control by maintaining steady suction of the waterpump, regardless of any increase or decrease of pressure in the water-line.

Strictly identical conditions were maintained during all measurements. The carbon black was previously extracted by acetone until the liquid flowing from the shell in the Soxhlet apparatus was absolutely colorless. Following such extraction the black was dried for five hours at 120°C ., and was pulverized before being placed in one of the arms of tube U, while the other arm was previously filled with glass wool. The black was then compressed to a steady volume by gently tapping the tube against a rubber stopper. The height of the layer of carbon black was maintained in the whole series of experiments at 10 cm.; and its diameter was 1.5 cm. Air saturated by the vapors of the particular liquid being tested (carbon tetrachloride) was passed through until approximately constant weight was reached. The gain in weight was less than 0.002 gram.

The temperature of the tube U was kept constant at about 20° . The temperature of water in the thermostat was kept strictly at $15^{\circ} \pm 0.2^{\circ}$, so that a constant concentration of vapors of the particular liquid was guaranteed. The temperature of the thermostat was made expressly lower than that of tube U to prevent 100 per cent saturation by the vapors, for such saturation would frequently cause condensation of vapor as fog in the black itself, resulting in abnormal results.

The first experiments were conducted with air saturated by vapors of carbon disulfide, benzene and carbon tetrachloride.

The results are tabulated below; the values are maximum adsorptions expressed as percentages by weight of the carbon black.

	CS ₂	CCl ₄	C ₆ H ₆
Thermatomic black	0.55	0.86	0.81
Micronex carbon black.....	9.7	11.6	10.1

In subsequent experiments only carbon tetrachloride vapor was used. In these experiments, which were carried out very precisely, the flow of air was 4 liters per hour; the concentration of carbon tetrachloride was 0.5845 gram per liter.

The results of the experiments are given below:

I. Active blacks obtained by incomplete combustion of natural gas		Maximum adsorption of CCl ₄ (per cent by weight)
Name		
Micronex		10.5
Spheron		14.2
Kosmobile-66		14.30
Carbomet no. 3.....		11.0
Dixie		11.60
Arrow		13.20
Super-Spectra		61.50
II. Active blacks obtained from materials other than natural gas		
Black-F		12.2
Durex-0 (Wegelin)		11.1
III. Acetylene black		
Mapec		8.4
IV. Thermic blacks		
Velvetex		0.64
P-33		2.44
Thermax		0.83
V. Blacks from natural gas obtained by incomplete combustion at high temperature		
Fumonex		2.50
Polish black "D".....		1.90
Polish black "E".....		2.40
VI. Lamp blacks		
Black "A"		3.10
Black "B"		2.80
Black "C"		2.60
Black 106 (Wegelin).....		2.90
Black Soft SBI.....		2.3

Discussion of the results:

The above table shows clearly the relation between adsorptive power of vapors carbon tetrachloride and the activity of the black toward rubber, except the Super-Spectra black (which is not used in the rubber industry), which has a tremendously higher adsorptive power than other varieties of black, reaching almost 62 per cent.

Active carbon blacks used in the rubber industry adsorbed 10.5 to 14.3 per cent of carbon tetrachloride. The adsorbing power of acetylene black, which was 8.4 per cent was about 20 per cent less than of the least adsorptive active black.

The soft, inactive carbons, which show still smaller adsorbing power, form a separate group. Thermic blacks, *e. g.*, Velvetex and Thermax, which are strongly graphitized, showed practically no adsorption. Thermic black, P-33, produced in such a way that agglomeration of the particles in the thermic process is avoided by dilution of the gas undergoing decomposition with gaseous reaction products showed a much greater adsorbing power, *i. e.*, 2.4 per cent. The same may be said about carbon-blacks produced by incomplete combustion of natural gas at high temperatures; the adsorbing power of these types of black is similar to that of P-33.

Lamp black showed an adsorbing power from 3.1 to 2.6 per cent. On the basis of these data, it is evident that there is a definite line of demarcation between active and inactive carbon blacks.

RÉSUMÉ

This article describes the results of an investigation which throws light on the relation between the adsorbing power of carbon black for carbon tetrachloride vapor and the activity of the carbon black in rubber.

A series of active carbon blacks was examined and it was found that the adsorption of carbon tetrachloride vapor is related to the activity of the carbon black. Active carbon blacks adsorb from 14.3 to 10.5 per cent of carbon tetrachloride and inactive blacks from 3.1 to 0.64 per cent of carbon tetrachloride.

It is evident, therefore, that this method can be adapted to the determination, in a simple way of the degree of activity of carbon black in rubber.

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[No mention is made, in the survey of the literature, of diphenylguanidine absorption measurements which have been published in "Columbian Colloidal Carbons", pages 105, 175 and 177. A comparison of the two sets of data shows that the values for carbon tetrachloride run practically parallel to those for diphenylguanidine. This is particularly evident from the tabulated comparison below.

Black	Carbon tetrachloride, values	Diphenyl- guanidine, values
Super-Spectra	61.5	42.5
Kosmobile-66	14.3	13.7
Spheron	14.2	13.2
Arrow	13.2	11.1
Micronex	10.5	12.0
Acetylene	8.4	3.9
Fumonex	2.5	2.5
Lampblack	3.1 to 2.3	2 to 12
P-33	2.4	1.8

Carbon tetrachloride behaves therefore in a manner almost identical with diphenylguanidine in this respect.—Ed.]